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CX. *On the Variation of the "Extinction" Voltages of certain types of Low Tension Discharge Tubes under Different Conditions.* By JAMES TAYLOR, B.Sc., A.Inst.P., Pemberton Fellow, and WILLIAM STEPHENSON, B.Sc., Armstrong College, Newcastle-on-Tyne*.

ABSTRACT.

THE paper contains a description and theoretical discussion of results on the measurements of the extinction or lower critical voltages of "Osglim" lamps and certain types of air discharge-tubes, when a charged condenser is connected across the electrodes, and a "flash" takes place.

The method used for measurement is that described in a previous paper (Taylor and Stephenson, Journ. Scien. Instrs. ii. No. 2, p. 50).

The sequence of phenomena in the "flash" or discharge is analysed into three sections:—

(1) The capacity (C microfarads) charged to a potential of E volts, is placed across the tube, and a field of potential is thus set up across the tube electrodes, and a Townshend current flows through the latter. If a quantity of electricity q_1 is used up in establishing the glow, the potential V across the tube when the actual glow begins is given by

$$V = E - \frac{q_1}{C}.$$

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(2) The condenser discharges now through the tube (glow discharge) down to the lower critical voltage V_b^0 . This lower critical voltage is given, on certain assumptions, by the relation,

$$V_b^0 = F + V_a',$$

where F is a constant and V_a' is the cathode fall of potential at the end of the "flash" period.

In cases where the full area of the cathode is employed in discharge, and the initial current is such as to give an abnormal cathode fall of potential,

$$V_a' = V_a + \phi(V, C),$$

where $\phi(V, C)$ is the "lag" of the cathode fall of potential at the end of the "flash" behind the normal cathode fall V_a . This becomes zero for normal current densities.

(3) At the end of the luminous period there is still a space-charge, etc. in the tube; this is cleared up, resulting in a quantity transference q_2 and a further reduction of the voltage across the condenser. We have therefore that the apparent lower critical voltage, as measured, is,

$$V_b' = V_b + \phi(V, C) - \frac{q_2}{C}.$$

It is shown that the experimental results are in general agreement with those predicted from theoretical considerations.

The least voltage required for production of a "flash" (for a capacity C across the discharge-tube electrodes) is shown to be given by

$$V_c' = V_c + \frac{q_1}{C},$$

where V_c is the normal sparking or upper critical potential.

Certain confirming experimental results for the "Osglim" lamp are given.

Introduction.

In a previous paper (Journ. Scien. Instrs. ii. No. 2, p. 50) the present writers put forward a method for the determination of the extinction voltages for low-tension discharge-tubes under different conditions of capacity and voltage across their terminals, and gave one or two illustrative results for the case of the neon lamp. In the investigation, a condenser of capacity C microfarads was charged to a

potential E volts, and then connected across the terminals of a discharge-tube; a "flash" occurred, and the potential across the condenser at the end of the "flash", that is to say, the extinction or lower critical voltage under the conditions of experiment, was determined. It was pointed out that the determination of this extinction or lower critical voltage for a discharge-tube carrying a steady current is a matter of simplicity (Shaxby and Evans, *Proc. Phys. Soc. Lond.* xxxvi. p. 253, 1924). Recently, however, the phenomenon of "flashing" of discharge-tubes has received a certain amount of investigation (Pearson and Anson, *Proc. Phys. Soc. Lond.* xxxiv. p. 204, 1922; Taylor and Clarkson, *Journ. Scien. Instrs.* i. p. 173, 1923-1924; *Proc. Phys. Soc. Lond.* xxxvi. p. 269, 1924; *Phil. Mag.* xlix. p. 336, 1925), together with some of its applications in other directions (O. v. Baeyer and W. Kutzner, *Z. f. Phys.* xxi. p. 46, 1924; Appleton, Emmeleus, and Barnett, *Proc. Cam. Phil. Soc.* xxii. Pt. 3, p. 434, 1924).

The theoretically-derived expression for the time period of "flash" involves the lower critical voltage, but it is the value of this critical voltage under the obtaining conditions (in which a charged capacity is across the tube terminals) that is involved, not the lower critical voltage under a steady current. These critical voltages may differ considerably (see A. G. Tarrant, *Proc. Phys. Soc. Lond.* xxxvi. p. 280 (discussion), 1924; also Taylor and Stephenson, *Journ. Scien. Instrs. loc. cit.*).

The method employed in the present experiments is such that the lower critical voltage is determined under the actual conditions of a "flash" when a condenser of known magnitude, charged to a known potential, is connected across the tube.

The object of the present paper is to examine, in a more or less general theoretical manner, such condenser discharges and to put forward some results obtained in the cases of the "Osgilim" lamp and air discharge-tubes.

Theoretical Investigation of the Variation of the Extinction Voltage V_b' .

One of us (Taylor) has put forward the following theoretical considerations of the problem:—

A condenser of capacity C microfarads is charged to a potential E volts, and is placed across the terminals of a low-tension discharge-tube. The following sequence of

phenomena will occur and may be conveniently divided into three sections:—

(1) A field of potential across the discharge-tube electrodes will be established, and if there is any ionization within the filling gas a Townsend current will flow (*cp.* Reiche, *Ann. der Phys.* lii. p. 4, 1917). If the potential across the tube rises to the upper critical voltage or sparking potential V_c , under these conditions, the current will increase by ionization by collision, and a space-charge with its concomitant phenomena will be established.

Let i be the magnitude of the Townsend current at a time t secs. from the instant when the condenser was placed across the tube terminals, then the total expenditure of charge in establishing the negative glow is given by,

$$q_1 = \int_0^{t_0} i \cdot dt,$$

where the integral is taken over the total time t_0 required to establish the glow. For a discharge-tube under constant conditions, and for capacities which are either fairly large (so that the whole of the cathode is covered with the negative glow) or of closely comparable magnitude, it would be expected that, for a constant ionizing agent (such as the γ -rays from radium bromide), q_1 would be approximately constant. It is evident, therefore, that the potential across the tube when the glow is just established is given by the relation,

$$V = E - \frac{q_1}{C} = E - \frac{\int_0^{t_0} i \cdot dt}{C} \dots \dots (1)$$

(2) The condenser now discharges through the tube down to the lower critical voltage V_b^0 , that is, the voltage at which the tube ceases to conduct in the form of a glow discharge.

If we assume that the lower critical voltage V_b^0 is of the value of the cathode fall of potential plus a voltage just sufficient to carry the ions over from the negative glow to the anode, we may write (Taylor and Clarkson, *Journ. Scien. Instrs.* i. No. 6, p. 173),

$$V_b^0 = F + V_a', \dots \dots (2)$$

where V_a' is the value of the cathode fall of potential at the end of the "flash" and F is a constant.

(3) At the end of the "flash" there is still a space-charge

and ionization in the gas within the tube. This space-charge, etc. will be cleared up very rapidly (in a time of the order of 10^{-6} sec.), but in the process there will have been a definite transference of electrical charge across the tube, and a further depreciation of the voltage across the condenser. Let this quantity be denoted by q_2 , and we have,

$$q_2 = \int_0^{t'} I \cdot dt,$$

where I is the instantaneous current at a time t seconds after the termination of the luminous discharge, and t' is the time required for the space-charge, etc. to be cleared up. The further diminution of the voltage across the capacity C is evidently

$$\frac{q_2}{C} = \frac{\int_0^{t'} I \cdot dt}{C},$$

so that the apparent lower critical voltage for the tube under these conditions is given by

$$V_{b'} = V_b - \frac{\int_0^{t'} I \cdot dt}{C} = V_a' + F - \frac{\int_0^{t'} I \cdot dt}{C}, \quad (3)$$

V_a' , F , and q_2 are complicated functions.

Further Consideration of Section (1).

It was shown that for the glow-discharge to be produced a quantity of electricity q_1 was transferred across the tube, and that the potential across the condenser after this transference was given by the relation of equation (1). Now, if $V < V_c$ (the upper critical voltage), which we are assuming to be a constant, no glow-discharge can be produced. We have evidently for a "flash" just to take place,

$$V_c = E - \frac{\int_0^{t_0} i \cdot dt}{C} \quad . \quad . \quad . \quad . \quad (4)$$

When the value of the capacity C is great (in these experiments usually of the order of 10^{-3} microfarad or more), the minimum value of E necessary for a glow-discharge to be produced is, within the limits of experimental error, of the value V_c , since the second term of equation (4) is small com-

pared with the first, for large capacities. When, however, C becomes small (10^{-3} microfarad and less in most experiments on "Osglim" lamps), the second term increases fairly rapidly, and the minimum voltage across the condenser required for a glow-discharge to be produced is given by

$$V_c' = V_c + \frac{\int_0^{t_0} i \cdot dt}{C} \dots \dots \dots (5)$$

If we can assume for these small values of C that the integral term of equation (5) is constant, it is evident that the graphs showing the relationship between V_c' and C will be hyperbolic in form. This is found to be approximately correct in experiments on the neon discharge-tubes.

Further Consideration of Section (3).

There are two cases to be distinguished :

(a) Where the current at the commencement of the luminous period is sufficiently great to give abnormal cathode falls of potential (H. A. Wilson, *Phil. Mag.* ser. 6, iv. p. 608, 1902).

(b) Where the current at the beginning of the "flash" is such as to give the normal cathode fall of potential (Wilson, *loc. cit.*). In the case of small capacities, a portion only of the cathode area is utilized in the luminous discharge, so that the current density may still be of the normal value.

Under the first heading is included the discharge through a tube when large capacities are employed, but it must be observed that the fact of abnormality of the cathode fall of potential is conditioned by the size of the cathode as well as by the magnitude of the capacity.

Let the cathode fall of potential be V_a^0 at the beginning of the "flash". The potential across the tube falls rapidly (the whole "flash" occupying a short fraction of a second only, as a rule), and there will be a "lag" of the cathode fall behind the normal value that would be attained if a sufficient time were allowed to elapse. (One may regard this "lag" as a "fatigue" or hysteresis effect.)

We may write, therefore, on certain assumptions (see Taylor and Clarkson, *Journ. Scien. Instrs. loc. cit.*),

$$V_b' = V_a' + F,$$

where V_a' is the value of the cathode fall of potential when $(V - V_a') = F$, the voltage just sufficient to carry the ions

over to the anode from the negative glow. V_a' will be some function of i , the initial current through the tube in the luminous period, and will thus depend largely upon V (see equation (1)) and the magnitude of C (see also Taylor and Clarkson, *Phil. Mag. loc. cit.*), so that we may write

$$V_a' = V_a + \phi(V, C),$$

where V is the voltage across the tube at the instant the glow-discharge begins. We have, further, from equation (3),

$$\begin{aligned} V_b' &= V_a + F + \phi(V, C) - \frac{\int_0^{t_1} I \cdot dt}{C} \\ &= V_b + \phi(V, C) - \frac{\int_0^{t_1} I \cdot dt}{C}, \quad \dots \quad (6) \end{aligned}$$

where V_b is the normal lower critical voltage (that is, the lower critical voltage when $V_a' = V_a$).

Now, when C is large, the last term of equation (6) is of negligible value compared with the others, so that the equation may be approximated to the form

$$V_b' = V_b + \phi(V, C). \quad \dots \quad (7)$$

When the value of the capacity C becomes such that the current through the discharge-tube never rises above the normal density value, the "lag" $\phi(V, C)$ becomes zero, we have $V_b' = V_b$, and the lower critical voltage should be independent of C over a wide range.

For smaller capacities the last term of equation (6) comes into prominence, and we have the following approximate relation holding:—

$$V_b' = V_b - \frac{\int_0^{t_1} I \cdot dt}{C}. \quad \dots \quad (8)$$

THE EXPERIMENTAL RESULTS.

Introduction.

A number of experiments were carried out using neon discharge-tubes in the convenient form of the well-known "Osglim" lamps. These lamps contain a filling-gas of about 75 per cent. of neon and 25 per cent. of helium (together with certain impurities, such as hydrogen and mercury vapour), at a pressure of approximately 10 mm. of mercury. The electrodes are of iron, the cathode being

in the form of some letter of the alphabet (or a "beehive" spiral of iron wire, in one type of the lamp), and the anode a small cylinder of iron, at a distance of one or two mm. from the cathode. There is no positive column in the discharge of these lamps, the light being emitted entirely from the negative glow (Ryde, *Phot. Journ.* June 1922).

In the experiments on the air discharge-tubes, a "beehive" "Osglim" lamp was improvised as a discharge-tube, by opening the nipple of the bulb and sealing on a glass tube so that the lamp could be attached to a Toepler pump and apparatus for evacuating. Phosphorus pentoxide tubes were employed for drying the air and the pressure was measured by a McLeod gauge.

In other experiments on the air discharge-tubes, a tube with parallel molybdenum-wire electrodes was used. This tube was the one used in experiments on the critical resistance for "flashing" of air discharge-tubes, described in a previous paper (Taylor and Clarkson, *Phil. Mag. loc. cit.*), where a description of the tube is given.

Previous to experimenting, the tubes were "overrun" so as to bring them into a more stable condition (Taylor and Clarkson, *Phil. Mag. loc. cit.*; also *cp.* Dubois, *C. Rend.* clxxv. p. 947, 1922), and overcome the trouble caused by "salient" points on the electrodes.

The Prevention of "Lag" in "Flashing."

The time "lag" in the occurrence of a discharge, behind the voltage tending to produce it, is a well-known phenomenon. In the present experiments a quantity of radium bromide in a sealed glass tube was used as external ionizing agent (the γ -rays being the effective ionizing radiations) (Taylor and Stephenson, *Journ. Scien. Instrs. loc. cit.*) to overcome the "lag" effects. In the case of the larger capacities (about 10^{-1} microfarad upwards) the value of the lower critical voltage, as determined experimentally, was found to be independent of the quantity of the radium bromide or its distance away from the tube, provided there was sufficient ionization produced to do away with the "lag." For the small capacities the results appeared to be independent of the quantity and distance of the radium bromide, but it was most difficult to get a discharge at all unless the radium bromide was in close proximity to the tube, and without its presence definite values of V_b' were not obtainable.

An interesting observation was made when using the parallel molybdenum-wire electrode discharge-tube. With

capacities of the order 10^{-3} microfarad and certain charging voltages, a discharge could be obtained when the radium bromide was removed to some distance, but when it was brought into close proximity to the tube no discharge could be obtained, the condenser charge being dissipated, presumably, by the "dark" discharge which precedes the luminous one.

Nature of the "Flashes."

In the "Osglim" lamps the full area of the cathode is employed in the discharge, for capacities greater than some 0.05 microfarad (this value varies somewhat, of course, with the type of lamp); but the intensity of the negative glow at the lower limits is exceedingly feeble. The intensity increases with the capacity C , and becomes very great for large capacities. In the case of the small capacities a part only of the cathode is illuminated by the negative glow during the luminous period. At values of C of the order of 10^{-4} microfarad a very minute portion of the cathode is utilized, and it is most difficult under such conditions to judge whether the type of discharge is normal.

When using the molybdenum-wire electrode tube, the full area of the electrode was employed down to very small capacities (about 0.004 microfarad), but the intensity of the glow decreased as the capacity diminished.

Abnormal Types of Discharge.

Several abnormal types of discharge were observed in the "beehive" air discharge-tube. Occasionally a "salient" point would crop up on the anode, and the discharge would be concentrated there as a sort of positive or anode glow, the intrinsic luminosity of the region of the "salient" point being very much greater than that of the usual negative glow. This type of discharge borders upon the arc discharge, and the value of the lower critical voltage V_b' is very much less than the normal, though precise determinations cannot be made because of the erratic nature of the discharge.

Further, in the case of the same tube at the lower pressures investigated (less than about 1 mm. of mercury), in some "flashes," instead of the usual diffuse negative glow a more intense discharge immediately around the anode was produced. Occasionally streamers from the anode were observed.

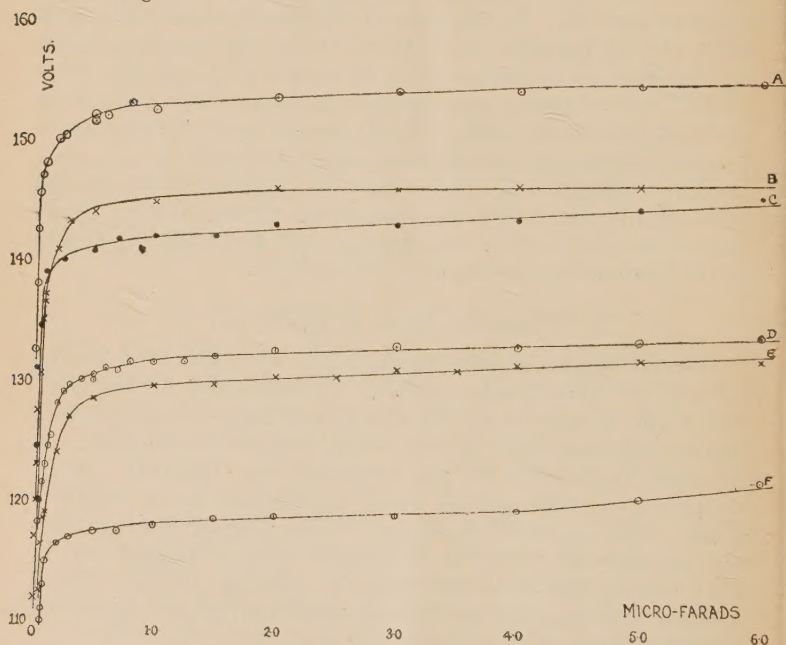
These abnormal types of discharge appear to be similar to some of those observed by Watson in neon and helium discharge-tubes (Proc. Cam. Phil. Soc. xvii. p. 90, 1913).

THE EXPERIMENTAL RESULTS FOR THE NEON
DISCHARGE TUBES.*The Variation of the Lower Critical Voltage with the
Capacity for a Fixed Charging Voltage.*

The variation of the lower critical voltage with the capacity for fixed charging voltages was investigated in the case of a number of types of the "Osglim" lamps. The general relations obtained were the same for all the different types.

The graphs of fig. 1 show the relations between the lower critical voltage V_b' and C for fixed charging voltage of

Fig. 1.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity for a Fixed Value of the Charging Voltage E.



GRAPH A.—"Osglim" lamp, "R" type. Not "overrun." External ionizing agent, radium bromide.

GRAPH B.—Do. after "overrunning."

GRAPH C.—"Osglim" lamp, "O" type. Not "overrun." External ionizing agent, radium bromide.

GRAPH D.—"Osglim" lamp, "R" type. "Overrun." External ionizing agent, radium bromide.

GRAPH E.—"Osglim" lamp, "Beehive" type. "Beehive" as cathode. External ionizing agent, radium bromide.

GRAPH F.—Do. "Beehive" as anode.

Charging Voltage E, 200 volts throughout.

TABLE I. (Graphs of fig. 1.)

Graphs showing Relationship between Lower Critical Voltage and Capacity, for a Fixed Value of the Charging Voltage E (200 volts).

| Capacity in μ F. | (A.) | (B.) | (C.) | (D.) | (E.) | (F.) |
|-------------------------|--------------|-------|-------|-------|-------|-------|
| 7.25 | ... | ... | 146 | 136 | 132 | 122.5 |
| 6.0..... | 155 | ... | 145.5 | 134 | 132 | 122 |
| 5.0..... | 154.5 | 148.3 | 144.5 | 133.5 | 132 | 120.5 |
| 4.0..... | 154 | 146.3 | 143.5 | 133 | 131.5 | 119.5 |
| 3.5..... | ... | ... | ... | ... | 131 | ... |
| 3.0..... | 154 | 146.0 | 143 | 133 | 131 | 119 |
| 2.5..... | ... | ... | ... | ... | 130.3 | ... |
| 2.0..... | 153.5 | 146.0 | 143 | 132.5 | 130.3 | 119 |
| 1.5..... | ... | ... | 142 | 132 | 129.7 | 118.5 |
| 1.25 | ... | ... | ... | 131.5 | ... | ... |
| 1.0..... | 152.5 | 144.8 | 142 | 131.5 | 129.5 | 118 |
| 0.8..... | 153.0 | ... | ... | 131.5 | ... | ... |
| 0.75 | ... | ... | 141.5 | 130.7 | ... | 117.5 |
| 0.6..... | 152.0 | ... | ... | 131 | ... | ... |
| 0.5..... | 152.0(151.5) | 143.8 | 140.7 | 130 | 128.5 | 117.5 |
| 0.4..... | ... | ... | ... | 130 | ... | ... |
| 0.3..... | ... | 143.2 | ... | 129.5 | 127 | 117 |
| 0.25 | 150.3 | ... | 140 | 129 | ... | ... |
| 0.2..... | 150 | 140.8 | ... | 128 | 124 | 116.5 |
| 0.154..... | ... | ... | ... | 125.5 | ... | ... |
| 0.135..... | ... | ... | ... | 124.5 | ... | ... |
| 0.10 | 148 | 137.2 | 139 | 123 | 119 | 115 |
| 0.083..... | 148 | 136.5 | ... | ... | 118.5 | 113 |
| 0.071..... | 147 | 135 | ... | 121.5 | 116.5 | 111 |
| 0.063..... | ... | 130.5 | 134.5 | 120.9 | ... | 110 |
| 0.05 | ... | ... | 134 | 120 | ... | ... |
| 0.046..... | 145.5 | 130.5 | ... | 118.2 | 112.5 | ... |
| 0.0315 ... | 142.5 | 127.5 | 131 | ... | ... | ... |
| 0.016..... | 138 | 123.0 | 124.5 | ... | ... | ... |
| 0.014..... | ... | 120 | ... | ... | ... | ... |
| 0.008..... | 132.5 | 115 | ... | ... | ... | ... |
| 0.005..... | ... | 112 | ... | ... | ... | ... |

(A.) "R₁" lamp. Not overrun. RaBr external ionizer.

(B.) do. After overrunning. RaBr external ionizer.

(C.) "O" lamp. Not overrun. RaBr; lamp in complete darkness.

(D.) "R" overrun lamp. RaBr.

(E.) "Beehive" lamp. Beehive as cathode.

(F.) do. do. anode.

200 volts, and several types of lamps (the description of the lamps is given in the fig.).

The following general results are apparent from a consideration of the graphs :—

(1) For large capacities above about 1 microfarad or so the graphs are approximately linear in C .

These portions of the graphs may be expressed by the general empirical relation,

$$V_b' = V_b + \beta \cdot C, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where β is some small constant for a fixed value of the charging voltage E .

(2) With capacities less than about 1 microfarad, the slope of the graphs begins to increase, at first slowly, and then quickly, and V_b' decreases rapidly as C is diminished. This is to be expected from equation (8). It is not possible, however, to treat this portion of the curves quantitatively,

because the function $\int_0^{t'} I \cdot dt$, which represents the quantity transference across the tube by the clearing up of the space-charge, etc., is certainly not constant for all capacities, for it is found, experimentally, that the intensity of the glow decreases with the capacity, and the actual area of cathode employed in discharge begins to diminish with the smaller capacities.

The function $\int_0^{t'} I \cdot dt$, need not be more than some 10^{-6} practical units, a value well within the probabilities of the case, to explain the magnitude of the V_b' variations.

Fig. 2 shows the similar relations for the smaller capacities (magnified capacity scale). It is observable that, except in the case of graph 1 where the cathode area is very small, the lower critical voltage attains a minimum at very small capacities, and appears to rise in value with further diminution of C . (It was sometimes difficult to decide whether V_b' was actually rising or merely stationary at these small capacities.)

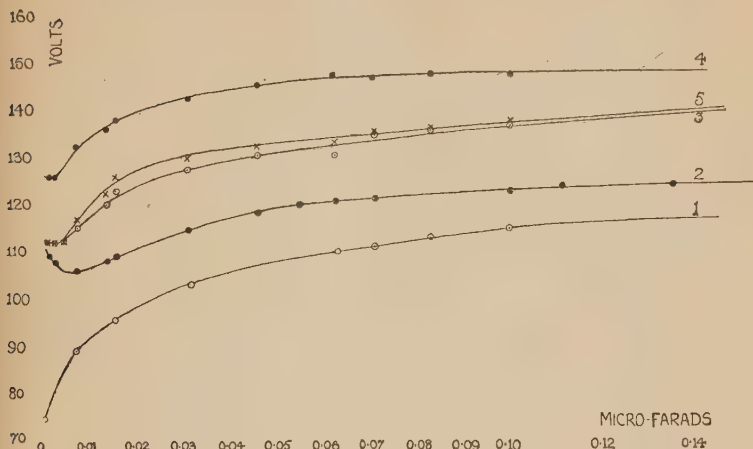
The minima of the graphs suggests that the ratio

$$\frac{\int_0^{t'} I \cdot dt}{C}$$

attains a maximum and then decreases as C is further diminished.

"Extinction" Voltages of Low Tension Discharge Tubes. 1093

Fig. 2.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity for a Fixed Value of the Charging Voltage E, for small Capacities,



GRAPH 1.—"Beehive" "Osglim" lamp. Not "overrun." Neon lamp used as external ionizing agent. "Beehive" as anode, Full cathode is used in discharge throughout, but intensity is very feeble for the smaller capacity values.

GRAPH 2.—"Osglim" lamp, "R" type. "Overrun." Radium bromide used as external ionizing agent. Less than full cathode used for capacities less than 0.04 microfarad (circa).

GRAPH 3.—"Osglim" lamp, "R" type. "Overrun." Radium bromide used as external ionizing agent. Full electrode used till about 0.01 microfarad.

GRAPH 4.—"Osglim" lamp, "R" type. Not "overrun." Radium bromide used as external ionizing agent.

GRAPH 5.—"Osglim" lamp. Same lamp as (4), but slightly "overrun." Radium bromide used as external ionizing agent.

Charging Voltage throughout, 200 volts.

TABLE II. (Graphs of fig. 2.)

Neon Lamp, Small Capacities.

NEON Lamp. E = 200 volts constant.

Graph 1.

"Beehive" lamp; not "overrun." Neon "I" lamp used as external ionizing agent; steady temperature condition. The small anode is used as cathode. E = const. 200 volts. Whole cathode is used throughout; discharge very feeble, however, for lowest capacity value.

Results:—

| | | | | |
|----------------------|-------|-------|-------|-------|
| C = 0.1 μ F | 0.083 | 0.071 | 0.063 | 0.046 |
| V _b '=115 | 113 | 111 | 110 | 107 |
| C = 0.032 μ F | 0.016 | 0.077 | 0.001 | |
| V _b '=103 | 95.5 | 89 | 74 | |

Graph 2.

"R" aged lamp. RaBr as external ionizing agent. E = 200 volts.
Not all the cathode is used at capacities less than 0.04 (circa).

| | | | | |
|--------------------------|--------|--------|-------|--------|
| C = 0.154 μ F | 0.135 | 0.111 | 0.071 | 0.062 |
| V _b ' = 125.5 | 124.5 | 124.5 | 121.5 | 121.0 |
| C = 0.055 μ F | 0.046 | 0.0315 | 0.016 | 0.0142 |
| V _b ' = 120 | 118.2 | 114.5 | 109.0 | 108.0 |
| C = 0.0077 μ F | 0.0033 | 0.0022 | | |
| V _b ' = 106 | 108 | 109 | | |

Graph 3.

"R₂" lamp. After "overrunning." E = 200 volts. RaBr.
Compare with 4 (below). Full electrode employed until 0.016 μ F.

| | | | | | |
|--------------------------|--------|--------|--------|--------|--------|
| C = 0.1 μ F | 0.083 | 0.071 | 0.062 | 0.0462 | 0.0315 |
| V _b ' = 137.2 | 136.5 | 135 | 130.5 | 130.5 | 127.5 |
| C = 0.016 μ F | 0.0147 | 0.0077 | 0.0056 | 0.0033 | |
| V _b ' = 123 | 120 | 115 | 112 | 112 | |

Graph 4.

"R₂" lamp. Before "overrunning." E = 200. RaBr.

| | | | | | |
|------------------------|--------|--------|--------|--------|--------|
| C = 0.1 μ F | 0.083 | 0.071 | 0.062 | 0.0462 | 0.0315 |
| V _b ' = 148 | 148 | 147 | 148 | 145.5 | 142 |
| C = 0.016 μ F | 0.0147 | 0.0077 | 0.0033 | 0.0022 | |
| V _b ' = 138 | 136 | 132.5 | 126 | 126 | |

Graph 5.

"R₂" lamp. RaBr ionizing agent. E = 200. Slightly "overrun."

| | | | | | |
|--------------------------|--------|--------|--------|--------|--------|
| C = 0.1 μ F | 0.083 | 0.071 | 0.062 | 0.0462 | 0.0315 |
| V _b ' = 137.2 | 136.5 | 135.5 | 133 | 132.2 | 130 |
| C = 0.016 μ F | 0.0147 | 0.0077 | 0.0033 | 0.0022 | |
| V _b ' = 123.5 | 122 | 117 | 112 | 112 | |

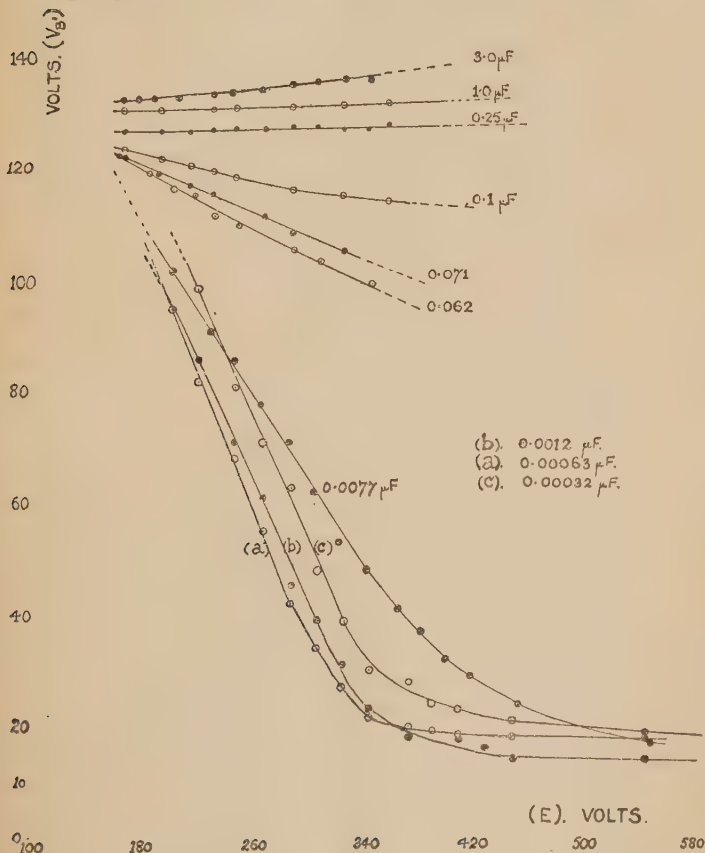
From equation (1) we see that V, the voltage across the discharge-tube at which the glow discharge begins, becomes less as C is decreased. It is found experimentally (see later) that the divergence of V from E only becomes grave at values of C of the order of 10⁻³ microfarad, consequently, since the the magnitude of the current at the commencement of the glow-discharge depends on V, the current magnitude will begin to fall off rapidly with diminution of C at capacities of the above order: concurrently, the area of the negative glow will diminish, thus diminishing the quantity transference in clearing up the space charge, etc. The above ratio may thus achieve a maximum and begin to decrease, so that, as is to be seen from a consideration of

equation (8), V_b' may increase again as the capacity becomes smaller.

The Variation of the Lower Critical Voltage with the Charging Voltage E for Fixed Values of the Capacity.

Fig. 3 gives a set of graphs showing the relationship between the lower critical voltage V_b' and the charging voltage E, for fixed values of the capacity C. The lamp used was an "Osglim" lamp of the letter "R" type.

Fig. 3.—Graphs showing the Relationship between the Lower Critical Voltage and the Charging Voltage E, for Constant Values of the Capacity C.



"Osglim" lamp. "R" type. "Overrun,"

or small capacities (a, b, c, etc.) only a small part of the cathode is used, except at 500 volts or more when the total area of the cathode is covered with negative glow during the discharge.

TABLE III. (continued).

| | | | | | | | | |
|----------------|-------|-----|-----------------|-----|------------------|----------------|-----|-----|
| 0.0077 μ F | 201 | 102 | 0.00063 μ F | 201 | 95 | 0.0012 μ F | 201 | 95 |
| | 229.5 | 91 | (a) | 220 | 82 | (b) | 220 | 86 |
| | 246 | 86 | | 246 | 68 | | 246 | 71 |
| | 265 | 78 | | 267 | 55 | | 267 | 61 |
| | 285 | 71 | | 287 | 42 | | 287 | 45 |
| | 304 | 62 | | 306 | 34 | | 306 | 39 |
| | 322 | 53 | | 324 | 27 | | 324 | 31 |
| | 342 | 48 | | 344 | 21.5 | | 344 | 23 |
| | 365 | 41 | | 373 | 20 | | 373 | 18 |
| | 382 | 37 | | 390 | 19 | | 390 | ... |
| | 399 | 32 | | 409 | 18.5 | | 409 | 18 |
| | 417 | 29 | | 428 | ... | | 428 | 16 |
| | 452 | 24 | | 448 | 18 | | 448 | 14 |
| | 549 | 17 | | 545 | 17.8 | | 545 | 14 |
| | | | C. | E. | V _b ' | | | |
| | | | 0.00032 μ F | 220 | 98 | | | |
| | | | (c) | 246 | 81 | | | |
| | | | | 267 | 71 | | | |
| | | | | 287 | 63 | | | |
| | | | | 306 | 48 | | | |
| | | | | 324 | 39 | | | |
| | | | | 344 | 30 | | | |
| | | | | 373 | 23 | | | |
| | | | | 390 | 24 | | | |
| | | | | 409 | 23 | | | |
| | | | | 428 | ... | | | |
| | | | | 448 | 21 | | | |
| | | | | 545 | 18.5 | | | |

GENERAL.

"R₁" lamp.—For small condensers (*a*, *b*, *c*, etc.) only a small part of the electrode is used, except at 500 volts or more, when nearly the whole cathode becomes covered with glow during the discharge.

Variation of V_c' with the Capacity C.

It was shown that the minimum charging voltage across the capacity, required for a glow-discharge to be produced, was given by the relation of equation (5). Fig. 4 shows the graphs obtained in the cases of two neon discharge-tubes. The graphs are approximately hyperbolic, graph (*a*) being represented by the empirical form (approximately)

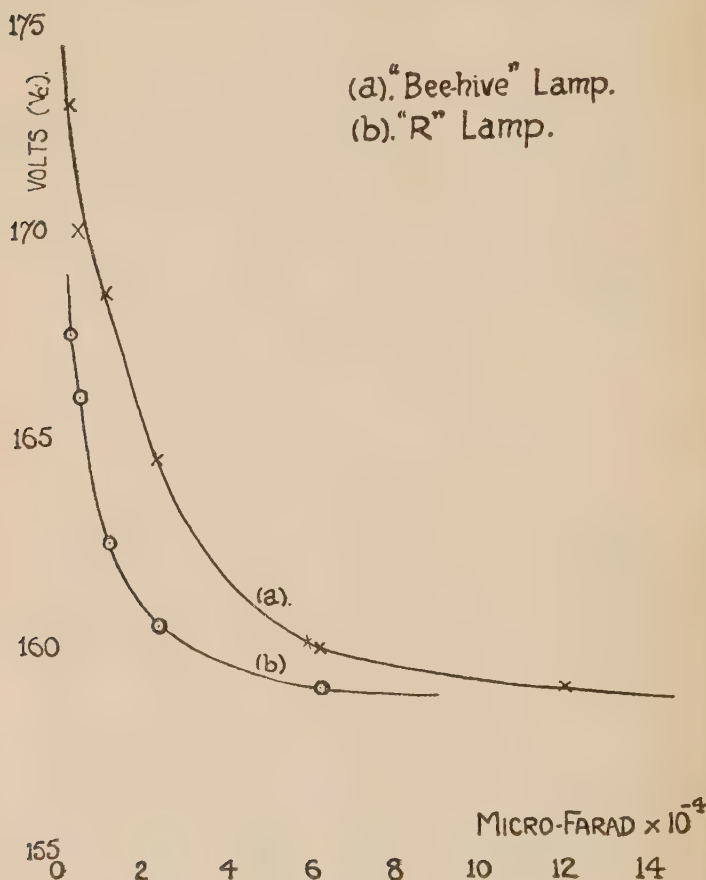
$$V_c' = 158.2 + \frac{11.3}{C}, \dots \dots \dots (10)$$

and graph (*b*) more exactly by

$$V_c' = 158 + \frac{6.0}{C} \dots \dots \dots (1')$$

It would appear, therefore, that the numerator of the second term of equation (5), which represents the quantity transference across the tube in establishing the glow discharge, is approximately constant, at least in the case of the

Fig. 4.— Graphs showing the Relationship between the Capacity C and the least Voltage V_c' required to produce a Glow-Discharge.



smaller capacities. The first terms of equations (10) and (11) are of the value of the normal sparking potentials for the tubes.

It has not been possible so far to perform similar experiments on the air discharge-tubes, but it is hoped to be able to do so in the near future.

TABLE IV.

"R" lamp. RaBr ionizing agent.

$$V_c' = 158 + \frac{6}{C}$$

| C. in μF . | V_c' . | |
|-----------------|----------|--------------|
| 0.00063 | 159 | <i>159</i> |
| 0.00025 | 160.5 | <i>160.4</i> |
| 0.000135 | 162.5 | <i>161.5</i> |
| 0.00007 | 166 | <i>166.5</i> |
| 0.00005 | 167.5 | <i>170.0</i> |

"Beehive" lamp. RaBr ionizing agent.

$$V_c' = 158.2 + \frac{11.3}{C}$$

| C. in μF . | V_c' . | |
|-----------------|----------|--------------|
| 0.0012..... | 159 | <i>159.2</i> |
| 0.00063 | 160 | <i>160.1</i> |
| 0.00025 | 164.5 | <i>162.7</i> |
| 0.000135..... | 168.5 | <i>168.4</i> |
| 0.00007 | 170 | <i>174.0</i> |
| 0.00005 | 173 | <i>180.6</i> |

C. in 10^{-4} units. Italic figures give theoretical curve.

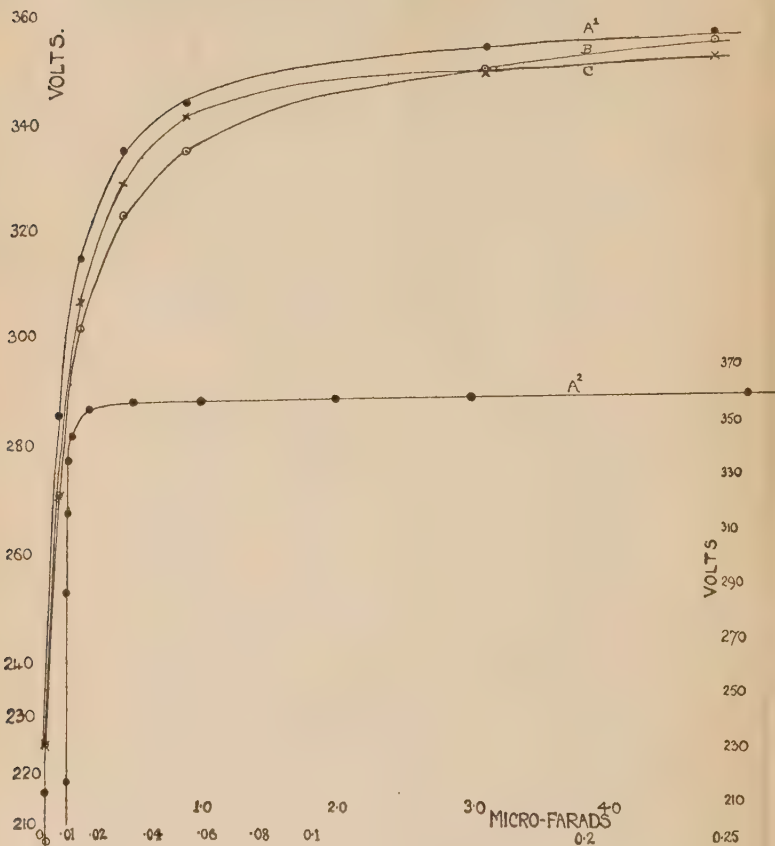
THE EXPERIMENTAL RESULTS FOR THE AIR DISCHARGE-TUBES.

The Variation of the Lower Critical Voltage with the Capacity for a Fixed Charging Voltage.

The variation of the lower critical voltage V_b' with the capacity for a fixed charging voltage was investigated in the case of the "Beehive" air discharge-tube at several different pressures. Fig. 5 shows the graphs of these relations, which are exactly similar to those obtained for the "Osglim" lamps (the actual values of the lower critical voltages are of course greater for the air discharge-tubes).

Owing to the lack of suitable capacities and batteries, it was not found possible to investigate the variation of V_b' with the charging voltage E over any great range of voltage, nor could it be determined whether there were minima for the V_b' , C graphs like those obtained with the "Osglim" lamps.

Fig. 5.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity, for a Fixed Charging Voltage E.



"Beehive" type of air discharge-tube.
 External ionizing agent, radium bromide.
 Charging Voltage E, 580 volts throughout.

GRAPH A².—Large Capacities (From $5\mu\text{F}$ maximum). Pressure 0.75 mm. Hg. Graph is typical, similar curves being obtained for pressure range 3 mm. to 0.2 mm.

GRAPH A¹.—Large capacity scale (Maximum $0.25\mu\text{F}$). Same results as graphed in A².

GRAPH B.—Similar to A¹, but pressure 2.92 mm.

GRAPH C. do. do. 1.67 mm.

TABLE V.

Air Discharge. "Beehive" lamp.

E = 580 volts. RaBr ionizing agent.

$p = (14.6 \times 0.02)$ cm. = 2.92 mm.

| | | | | | | |
|------------------------|-----|-----|-----|-----|-----|------|
| C = 5.0 μ F | 4.0 | 3.0 | 2.0 | 1.0 | 0.5 | 0.25 |
| V _b ' = 365 | 365 | 365 | 365 | 361 | 358 | 355 |

| | | | | | | |
|------------------------|-------|--------|-------|--------|--------|--|
| C = 0.166 μ F | 0.055 | 0.0315 | 0.016 | 0.0077 | 0.0022 | |
| V _b ' = 350 | 335 | 323 | 302 | 271 | 208 | |

E = 580 volts. RaBr ionizing agent. Air.

$p = (16.65 \times 0.01)$ cm. = 1.665 mm.

| | | | | | | |
|------------------------|-----|-----|-------|-------|-------|------|
| C = 5.0 μ F | 4.0 | 3.0 | 2.0 | 1.0 | 0.5 | 0.25 |
| V _b ' = 362 | 362 | 359 | 356.5 | 356.5 | 356.5 | 352 |

| | | | | | | |
|------------------------|-------|--------|-------|--------|--------|--|
| C = 0.166 | 0.055 | 0.0315 | 0.016 | 0.0077 | 0.0022 | |
| V _b ' = 349 | 341.5 | 329 | 307 | 271 | 225 | |

E = 580 volts. RaBr ionizing agent.

$p = (7.45 \times 0.01)$ cm. = 0.745 mm.

| | | | | | |
|------------------------|-----|-------|-----|-------|-------|
| C = 5.0 μ F | 3.0 | 2.0 | 1.0 | 0.5 | 0.25 |
| V _b ' = 360 | 358 | 357.5 | 357 | 356.5 | 356.5 |

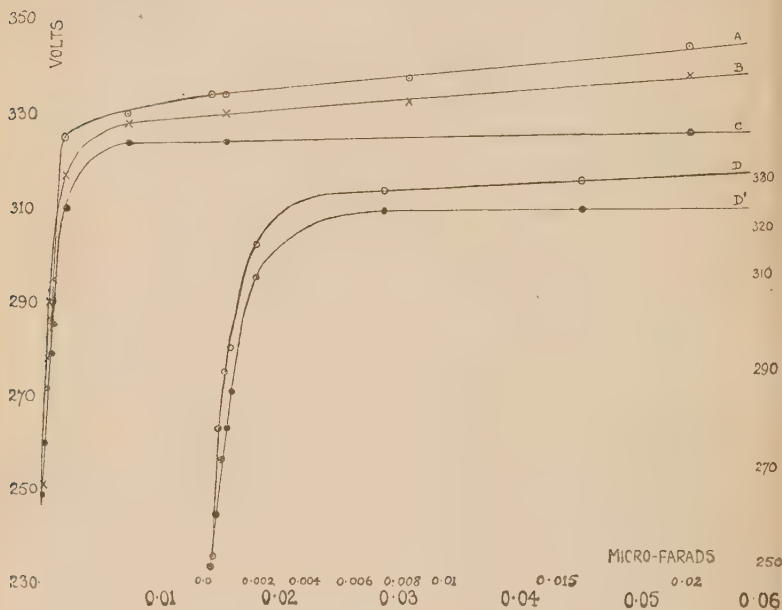
| | | | | | |
|------------------------|-------|--------|-------|--------|--------|
| C = 0.166 μ F | 0.055 | 0.0315 | 0.016 | 0.0077 | 0.0022 |
| V _b ' = 354 | 344 | 335 | 315 | 286 | 216 |

Similar relations were found to hold for the molybdenum-wire electrode discharge-tube (see graphs of fig. 6). The conductivity of the tube is, however, much less than the conductivities of the other tubes, because the area of the cathode is very small. The capacity range of abnormal cathode fall extends consequently much further into the region of small capacities. Indeed, for capacities greater than some 0.2 microfarad, the actual time duration of the discharge becomes considerable and the conditions for accurate performance of the present method break down. (The time of "flash" becomes comparable with the time period of the ballistic galvanometer employed, and an initial "kick," always in the same direction, inhibits results (see Taylor and Stephenson, Journ. Scien. Instr. *loc. cit.*).)

It is observable that V_b' in the case of this tube diminishes slowly with the capacity down to about 0.004 microfarad, when rapid diminution with the capacity ensues. In previous experiments on the variation of the critical resistance for

"flashing" (R_c) for this particular tube (see Taylor and Clarkson, *Phil. Mag. loc. cit.*) it was found that the critical resistance R_c decreased slowly and almost linearly with the capacity down to a capacity of 0.004 microfarad, when rapid diminution of R_c with further capacity reduction set in. The variation of the critical resistance is thus intimately connected with the variation of V_b' .

Fig. 6.—Graphs showing the Relationship between the Lower Critical Voltage and the Capacity, for a Fixed Value of the Charging Voltage E .



Air discharge-tube. Parallel molybdenum-wire electrodes tube.
External ionizing agent, radium bromide.
Charging Voltage E , 720 volts throughout.

GRAPH A.—Pressure 2.54 mm. Small capacity scale (maximum 0.055 μF).

GRAPH B.—Pressure 1.72 mm.

GRAPH C.—Pressure 1.13 mm.

GRAPH D.—Results for 1.72 mm. (graph B), but with enlarged capacity scale (0.02 μF).

GRAPH D'.—Results for 1.13 mm. (graph C); enlarged capacity scale.

TABLE VI.

Molybdenum Wire Electrode—Air.

E = 720 volts.

| Graph (A). | | | Graphs (B) (& D). | | |
|-----------------------------------------|----------------|----------|------------------------------------------|----------------|----------|
| <i>p.</i> | C. in μ F. | V_b' . | <i>p.</i> | C. in μ F. | V_b' . |
| { 12.7 \times 0.02) cm. = 2.54 mm. | 0.055 | 343 | { (17.2 \times 0.01) cm. = 1.72 mm. | 0.055 | 337 |
| | 0.0315 | 337 | | 0.0315 | 332 |
| | 0.016 | 334 | | 0.016 | 330 |
| | 0.0147 | 334 | | | |
| | 0.0077 | 330 | | 0.0077 | 328 |
| | 0.00223 | 325 | | 0.00223 | 317 |
| | 0.0012 | 290 | | 0.0012 | 295 |
| | 0.0010 | 286 | | 0.00093 | 290 |
| | 0.00063 | 286 (?) | | 0.00063 | 278 |
| | | | | 0.00039 | 251 |

Graphs (C) (& D¹).

| <i>p.</i> | C. in μ F. | V_b' . |
|-----------------------------------------|----------------|----------|
| { 11.3 \times 0.01) cm. = 1.13 mm. | 0.055 | 325 |
| | 0.016 | 324 |
| | 0.0077 | 324 |
| | 0.00223 | 310 |
| | 0.0012 | 285.5 |
| | 0.0010 | 278 |
| | 0.00075 | 271.5 |
| | 0.0005 | 260 |
| | 0.00028 | 249 |

We are indebted to Prof. G. W. Todd, of Armstrong College, under whose supervision the experiments were carried out, and to the Department of Scientific and Industrial Research for the grant which has enabled one of us to undertake the work.

CXI. *The Use of Commercial Plates in Research on the Latent Photographic Image.* By F. C. TOY, D.Sc., F.Inst.P. (Communication No. 44 from the British Photographic Research Association Laboratories)*.

THE fundamental importance of the photochemical law of the silver halide grain was recognized by Svedberg (*Zeitsch. wiss. Phot.* 1920, xx, p. 37) and Slade and Higson (Proc. Roy. Soc. 1920, 98 A, pp. 154-170) about the same time. Slade and Higson investigated the relation between the number of grains made developable, the time of exposure, and the intensity of the light. They used plates containing only a single layer of grains, so that these were all similarly situated as regards the incident light. Calling a the total number of grains present, and x the number made developable, they arrived at certain conclusions regarding the relation between

$$\log_e a/(a-x)$$

(which we will call n), the light intensity I , and the time of exposure t .

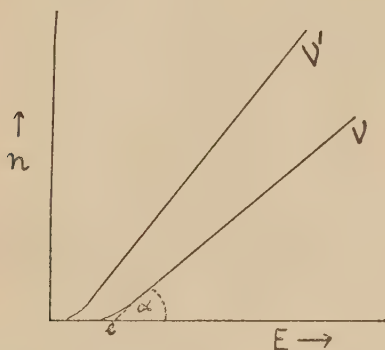
It is unnecessary to discuss their result in detail here; the main conclusion from their work was that the relation between n and I was expressed by an equation completely different in type from that which connected n and t . The results of much later work in the British Photographic Research Association laboratories has not confirmed this wide difference, and only partially confirmed the actual relationships which were found. Further, it has been found that a relationship which holds for one emulsion is not necessarily exactly the same for another, and this is the main difficulty in the way of establishing exact quantitative relations between the photographic effect and the conditions of exposure.

Since Slade and Higson's paper was written, it has been realised that the quantity we have called n is of great significance, in that it is actually the numerical measure of the number of reduction centres (expressed as average number per grain) which are formed by the light. This has led to many laborious experiments on the relation between n and the exposure, and for many emulsions it has now been shown that the curve connecting n and E ($E=I \times t$, where I or t is variable), for monochromatic light and

* Communicated by Dr. T. Slater Price, O.B.E., D.Sc., F.R.S.

normal exposures, is similar to those shown in fig. 1. There is a distinct "period of induction" followed by a rapid increase of dn/dE from zero to a constant value when the straight line portion is reached. The top of the curve need not be considered here, since the greater part of the photographic effect is produced while n is still on the straight line portion. It has been shown that the curved foot to the straight line is short compared with the range over which the straight line itself extends, and the object of this paper is not affected if we make the approximation that the straight line continues down to the exposure axis, cutting this at a value of the exposure which may be called the inertia

Fig. 1.



value (e). If α be the angle the straight line makes with the E axis, the equation connecting n and E may be written

$$n = \phi(E - e)$$

where $\phi = \tan \alpha$, and e = inertia value of exposure.

Taking this equation as the starting point, consider the general case of two monochromatic lights of frequency ν and ν' . Let these frequencies be such that the light absorption by the silver bromide grain is very much greater for ν' than for ν . This means that for equal incident energy of each light, more photographic effect is produced by ν' than by ν (Phil. Mag. xlviii. pp. 947-961 (1924)) and the curves for the two lights will be as shown in fig. 1.

The equations for these will be

$$n = \phi(E - e),$$

$$n = \phi'(E - e'),$$

where $e > e'$ and $\phi' > \phi$.

Now apply this result to a consideration of the effect produced in a *thick layer* of emulsion as it occurs on ordinary commercial plates. We will consider the emulsion divided into a large number of layers, each so thin that it may be considered to behave very nearly like a single layer. As the light penetrates the film, the intensity will decrease, the rate of decrease being much greater for ν' than for ν , since the silver bromide absorbs the former much more strongly (according to our assumption).

Let p and q be the ratios of the intensity transmitted to that incident upon any layer, for the lights ν and ν' , respectively, that is, p and q are the transmission factors of a layer. We will assume p and q are constant throughout the thickness of the emulsion*.

If the incident intensity is I , then, for ν , the intensities incident on successive layers will be

$$I, pI, p^2I, \dots$$

and for ν'

$$I, qI, q^2I, \dots$$

Let the plate be given an exposure $E (=I \times t)$. Then applying the law for the single layer to each layer in succession the total number of centres (N) formed will be, by the light of frequency ν ,

$$N = n_1 + n_2 + n_3 + \dots = \phi(E - e) + \phi(pE - e) + \phi(p^2E - e) + \dots \quad (1)$$

and by the light ν'

$$N' = n_1' + n_2' + n_3' + \dots = \phi'(E - e') + \phi'(qE - e') + \phi'(q^2E - e') + \dots \quad (2)$$

The first term in each of these expressions gives the number of centres formed in the top layer only. If the

* Abney showed (Camera Club J. p. 173, 1899) that the effective opacity of each layer is *lower* than that of the one above it in the series. Bloch and Renwick confirmed this (Phot. J. lvi. pp. 49-66, 1916) and came to the conclusion that the correct relation between the density (D) and the weight of silver bromide per unit area (W) of plate, was expressed by an equation of the type $D = aW^b$, where a and b are constant, b being < 1 . If the absorption for each layer of silver bromide were the same, b should be 1, instead of less as proved by Bloch and Renwick. They only determined the values of b in one case using monochromatic light and found it to be 0.82. The approximation made in the paper does not, however, affect the general result, which depends essentially on the fact that the terms in q (equation 2) decrease much more rapidly than the corresponding terms in p (equation 1).

exposure is very small, so that E is just greater than e , but $pE < e$ and $qE < e'$, then all the terms except the first are negative, implying physically no photographic effect in either case except in the first layer. With all exposures less than this value, the ratio of the numbers of centres produced by the two lights is given by

$$N'/N = \frac{\phi'}{\phi} \times \frac{(E - e')}{(E - e)}$$

which becomes infinite when $E = e$. This is, of course, expressed by curves in fig. 1. As the exposure is increased the light penetrates deeper into the film, and centres are formed in other layers than the first; that is, other terms than the first contribute their share to the total effect produced. The value of the successive terms added will depend on the values of p and q . In the case we have taken, the light of frequency ν' is much more strongly absorbed than ν , so that the transmission factor q is much less than p . Each of these being a fraction less than 1, the terms in q will decrease much more rapidly than the corresponding terms in p . At a certain term, say the $(r+1)$ th, $q^r E$ is less than e' , while $p^r E$ may still be considerably more than e , that is, more terms of equation 1 than 2 must be taken to get the total effect due to the incident intensity. In fact, as the exposure is increased and the light produces effects deeper down in the emulsion, N may become greater than N' , that is, *the relative effects produced in a layer of emulsion may be completely reversed if the thickness of the layer is varied.*

The usual and simplest effect to observe in a single-layer plate is the percentage of grains which are made developable, and this is easily obtained if the number of centres produced is known (Phil. Mag. xlv. pp. 352-371 (1922)). If x is this percentage, the values of the percentages for the different layers are given by

$$\left. \begin{aligned} x_1 &= 100(1 - e^{-n_1}) \\ x_2 &= 100(1 - e^{-n_2}) \\ &\dots \dots \dots \end{aligned} \right\}, \quad \dots \dots \dots (3)$$

where n_1 and n_2 , etc., are the average number of centres per grain in a single layer, and x_1 , x_2 , etc., the corresponding percentages changed. To obtain the percentage of grains changed in each layer of the emulsion, each term in n in

equations 1 and 2 must be converted separately to the corresponding x term by means of equation 3.

If we consider that we are examining an area of plate such that there are 100 grains in each layer, the addition of the terms in x will give us relative values of the total number of developed grains in all layers. If we call X and X' the total number of developable grains throughout the whole thickness of emulsion for ν and ν' respectively, we get finally from 1, 2, and 3

$$X = x_1 + x_2 + x_3 + \dots = 100 \{ (1 - e^{-\phi(E-e)}) + (1 - e^{-\phi(pE-e')}) + (1 - e^{-\phi(p^2E-e')}) + \dots \}. \quad (4)$$

$$X' = x'_1 + x'_2 + x'_3 + \dots = 100 \{ (1 - e^{-\phi'(E-e')}) + (1 - e^{-\phi'(qE-e')}) + (1 - e^{-\phi'(q^2E-e')}) + \dots \}. \quad (5)$$

As an example, let us take a case which has been investigated in our laboratory, viz., that of the effects produced by the blue line ($\lambda = 4358 \text{ \AA}$) and the ultra-violet line ($\lambda = 3650 \text{ \AA}$) of the mercury arc. The following values of the factors given in equations (1) and (2) are of the order of those actually found for the two frequencies mentioned, in the case of a pure bromide emulsion with small even grains:

$$\phi = 0.5, \phi' = 2.0; \quad e = 0.5, e' = 0.1; \quad p = 0.8, q = 0.5.$$

The value of the exposure is given in units of 1.2×10^{-6} calories per sq. cm. Using these data, it is easy to calculate the values of X and X' from equations (4) and (5) for the various values of E . These are given in the table and plotted in fig. 2.

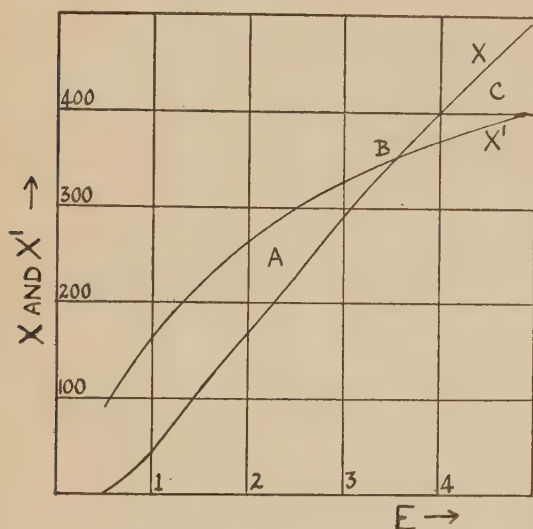
It will be seen at once, that for a thick layer of emulsion the relative effects produced by ν and ν' will depend on the exposure; thus if $E = 0.5$, $X'/X = \infty$ and this gradually decreases with increasing exposure until $X' = X$ when $E = 3.5$. For bigger values of E , X becomes greater than X' .

| E. | Total grains changed in all layers. | |
|-----------|-------------------------------------|-----|
| | X. | X'. |
| 0.5 | 0 | 88 |
| 1.0 | 43 | 169 |
| 2.0 | 172 | 267 |
| 3.0 | 293 | 336 |
| 4.0 | 398 | 364 |
| 5.0 | 492 | 399 |

This point has been tested experimentally using the same

frequencies as above, and thick plates of the same emulsion as gave the curves in fig. 1. Two strips of the same plate were exposed behind a wedge to known intensities of the blue and ultra-violet, the gradation of the wedge for each light being known. From this it is easy to calculate the intensities on the plate at every point, and the density after development of these points can be easily measured. Now we know that, at any rate approximately, the density of a developed silver image is proportional to the quantity of silver present, that is, to the total number of developed silver grains (assuming uniformity of grain size), so that if we plot density against intensity for each light we should

Fig. 2.



get curves similar to those obtained theoretically in fig. 2. That this is so is seen very clearly from fig. 3 and fig. 4, which give similar curves, one being obtained by varying the time and keeping the intensity constant, and the other by varying the intensity.

It should be pointed out that this kind of result would not necessarily be observed with *any* different monochromatic lights since it depends essentially on the great difference between p and q , which in turn depend on the great variation, with frequency, in the light absorption by the silver bromide. If the frequencies used were in a range of the spectrum over which the silver bromide absorption was

constant, the curves shown in figs. 3 and 4 would not be obtained, and the light which gave the greater effect on a single-layer plate would also give the greater effect on a thick layer, whatever the exposure.

Fig. 3.

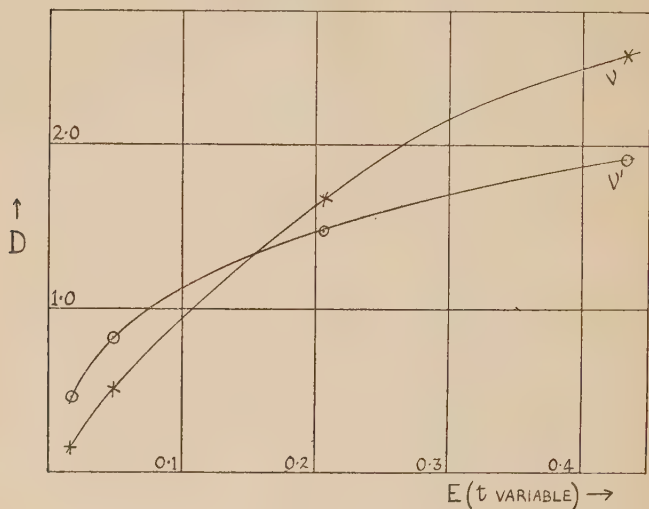
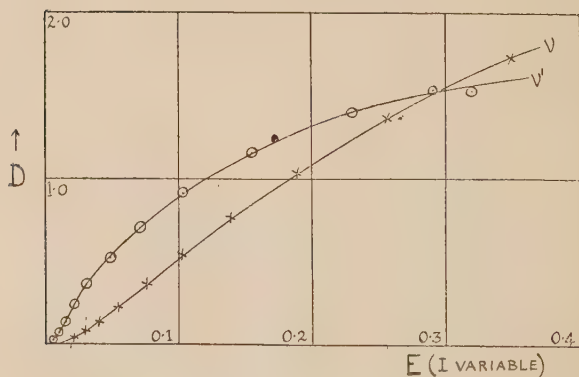


Fig. 4.



It follows that it may be exceedingly dangerous to use ordinary thickly coated commercial plates for experiments on the quantity of energy of different frequencies necessary for the formation of the latent image. This, however, has

recently been done by Helmick (J. Opt. Soc. Amer. ix. pp. 521-540 (1924)). Using four radiations of wavelengths 3650, 3131, 2653, 2537 Å., Helmick investigated the relation between the total energy incident and the total number of developable grains produced *throughout the whole thickness of the emulsion coating*. Knowing these, he has calculated the average number of quanta per grain which are required to make one grain developable. He found that, on the average, the number of quanta required for this purpose decreased as the frequency of the light decreased, and drew the conclusion that the efficiency of light quanta in producing developable grains increases as the frequency decreases.

Now, as far as is known, the variation of the light absorption by silver bromide with frequency has never been investigated over the range of frequencies used by Helmick, so that it may either be constant or it may vary enormously as we know it does in the visible and near ultra-violet. Slade and Toy (Proc. Roy. Soc. 97 A, pp. 181-190 (1920)) have shown that it is increasing very rapidly with increase of frequency from the visible down to about 3400 Å., the limit of their investigation.

The point is that Helmick's result is meaningless without a knowledge of the silver bromide absorption curve in the region employed by him. For, if this absorption does vary very rapidly with frequency in that region, and if, for the emulsion he used, the same relation holds between n and E as holds for the emulsion used here (as it probably does) the blackening curves for the different lights would be similar to those we have obtained here (though they would be reversed in order if the absorption were decreasing with increase of ν instead of increasing), with the result that *the conclusions drawn as to the relative efficiency of different frequency quanta would depend on the purely arbitrary exposure given to the plate*. Thus, if Helmick's exposures were such as to be in the region of A in fig. 2, he would have found that more grains were made developable by the light of greater frequency, and would have concluded that the efficiency of quanta as regards the formation of developable grains increased with the frequency. If he had given to his plate exposures corresponding to the region marked B in fig. 5 he might have concluded that the quanta of different frequencies were equally efficient, while at an exposure such as C the order of efficiency would have been completely reversed.

All this points to the necessity for using single-layer plates

for all accurate work on the relation between the energy required for the formation of the latent image and the frequency. Under such conditions there is as yet no evidence sufficiently definite for us to draw any other conclusion than that, per quantum absorbed, all frequencies of ultra-violet light are equally efficient in making developable the silver halide grain.

In conclusion, the author wishes to express his thanks to Dr. Slater Price for the interest which he has shown in this work.

CXII. *The Combustion of Carbon-Monoxide Mixtures.* By J. H. CROWE, M.Sc., and A. H. NEWAY, M.Sc., *Bowen Research Scholar* *.

IT has long been recognized that the Air standard cycle, as representing the ideal efficiency for an Internal Combustion Engine, is only permissible because of the lack of precise knowledge concerning the physico-chemical phenomena taking place during combustion. The Air standard postulates an "ideal air" with constant specific heat, and assumes that, in a mixture of this air and combustible gas, heat is added instantaneously, and, further, that during combustion there is no dissociation of the products.

The present investigations, which are part of a series undertaken at the Birmingham University, are an attempt to determine something of the manner in which combustion proceeds when a mixture is exploded in a closed vessel, more particularly to measure the velocity of propagation of the flame front. The apparatus necessary has been rather considerable, and this was designed and constructed by J. L. Pearson and R. C. A. Anderson. To the former is due the credit of developing the method of attacking the problem.

In order to simplify the conditions and eliminate wall action, the explosion vessel is a sphere of 16 inches diameter, and ignition is effected at the centre. The original method suggested for recording the passage of the flame was first put forward by J. D. Morgan ('Engineering,' October 1919). This consisted of having an insulated gap formed by two steel electrodes in the path of the flame, and in series with this a second gap for recording purposes and a condenser of suitable value. When the first gap is bridged by the

* Communicated by Prof. F. W. Burstall, M.A., M.Sc.

flame, the condenser is discharged and the spark at the other gap can be recorded photographically.

This arrangement will work very well when a bunsen flame is flicked through the gap, but when tried in the sphere it failed completely. After much experimental work the present method was developed, and this is essentially as follows.

The condenser is replaced by a motor alternator, the voltage of which is transformed up to about 8000. One side of the transformer is earthed, and the other side is connected through a variable liquid resistance to the external adjustable gap. Connexion is made from this to the central electrode of a large specially designed sparking-plug, which is screwed to the sphere. The sphere, and therefore the plug, is earthed. The cable connecting the two gaps has a certain capacity to earth, and, if the external gap is closed down slowly when the high voltage is on, a charging current can be made to flow and give a continuous discharge through the gap, while the gap in the sphere is in no way affected. When the flame reaches the points of the plug an arc is struck at both gaps, and the change from the capacity spark to the arc is plainly photographed on a falling plate. A more detailed description of some of the components of the apparatus can now be given.

The sphere is a mild steel forging, 16 inches in internal diameter, with walls $1\frac{1}{2}$ inches thick, and was machined from the solid. The two halves are bolted together by 18 $1\frac{1}{2}$ -inch nickel steel bolts. There are 24 plug-holes disposed along different radial lines, although only 17 plugs, including the firing plug, are used. In each hemisphere there are two inlet passages. One valve opens to a mercury U-tube and vacuum-pump, one is connected to the compressed-air bottle, another controls the gas (and oxygen when used), and the fourth one opens to the atmosphere and is also used for passing hot air through the sphere after an explosion. The inside surface of the sphere is silver-plated, as it had been found that, when using coal-gas, considerable corrosion took place, owing to the deposition of moisture.

The internal gaps which project into the sphere are arranged by screwing steel electrodes of varying lengths into the base and central spindle of large sparking-plugs, which were specially made by Messrs. Lodge Plugs Ltd. The electrodes and bases of the plugs are silver-plated. The gap at the points is normally 5 mm., but this is raised somewhat depending on the initial pressure used. The plug

having its points at the centre of the sphere is used as the ignition-plug and has a much smaller gap. Ignition is effected by means of a 6-volt accumulator and 6-inch trembler induction-coil. In order to time the firing of the charge at the right moment, an extra switch in the primary of the coil is arranged—a wiper switch on the plunger of the falling-plate camera.

There are five external gaps, and these are contained in a light-tight box, with a lens behind each to focus the capacity spark or arc on to the falling plate. The electrodes of each gap are carried in a frame of ebonite, the top one being fixed into an ebonite screw to give vertical adjustment. Focussing adjustment is also provided. Only three of the gaps are used, one being in series with the particular plug required and another in series with the firing plug, so that the ignition-spark is also recorded on the plate. The purpose of the third gap will be explained later.

The falling-plate camera is the standard camera made by The Cambridge Scientific Instrument Co. Ltd. The plate is released by an electro-magnetic catch and falls at a uniform speed controlled by a plunger working in an oil cylinder. The camera-box makes a light-tight joint with the external gap-box.

The time is put on to the plate by means of a vibrating bar time-marker, also a standard instrument. The bar is vibrated electrically, and drives a small synchronous motor having a spoked disk on the end of the armature. Light from an arc lamp passes through an aperture on to the falling plate, and the light is cut off regularly by the spokes, giving a line on the plate broken in hundredths of a second.

Besides measuring the flame velocity, a pressure record is taken on the same plate. For this purpose a Burstall Optical Indicator is fitted (for description see *Proc. Inst. of Mech. Eng.* 1923). The piston has been replaced by a diaphragm. This has two corrugations in it and is cut out of the solid, so that it is perfectly encastre, thus reducing any hysteresis effect.

In order to save time in the experimental work, a fan is used to stir up the mixture before firing. The fan spindle passes through the body of a plug screwed into the sphere and is driven at 800 r.p.m. by a small motor. The initial pressure is taken by a packing of lead shavings, and the explosion pressure by screwing back the spindle on to a seating on the plug after the fan has been stopped. The fan-blades, which are silver, are hinged on to the boss in order

to pass the $1\frac{1}{4}$ -inch hole, and when in action are close to the inner wall, so as not to affect the progress of the flame. The remaining exposed parts are all silver-plated.

An electric heater also screws into the sphere. This helps to drive off any moisture that may be deposited, and also to adjust the initial temperature if required.

The only combustible gas that has been used is carbon monoxide, and a small plant was put down for its manufacture. The gas is prepared by the usual laboratory method, the action of concentrated sulphuric acid on formic acid, the temperature being about 100°C . The gas is collected in a 6 cu. ft. holder and from there drawn off by a portable two-stage compressor into a storage-bottle. An oil separator is interposed between the compressor and the bottle, the gas passing up through a spiral of wire and any oil that has been sent over is deposited and run off. As used, the gas is saturated and the air is in the normal hygrometric state as it would be in gas-engine practice. The purity of the gas is 97.5 per cent., the remainder being air.

In order to obtain a complete record of the flame, twelve explosions for any set of conditions are necessary (only twelve plugs are available). After each explosion the sphere is exhausted and hot air passed through. After a second exhaustion, the air and gas are admitted very slowly in the correct proportions. The U-tube is used for pressure up to three atmospheres, and above this a Bourdon gauge. The mixture is then stirred for 20 minutes, which was found to give complete diffusion, and then left for a few minutes for eddies to die down. After the time-marker and indicator have been put on, the high voltage is switched on and the external gaps adjusted to give a continuous spark discharge. The mixture is then exploded by dropping the plate.

A vast number of difficulties with the apparatus presented themselves at first, but these have gradually been eliminated until experiments can now be carried out fairly continuously, although by no means rapidly. A considerable number of results were discarded before those given here were obtained. These can be repeated and the same results obtained within the limits of the small errors introduced in the proportions of gas to air, etc.

In the course of the preliminary experiments some information was obtained of the effect of diffusion on the manner of the flame spread. In one experiment the fan was only left on for five minutes. It was afterwards found that 20 minutes is necessary to obtain diffusion sufficiently

TABLE I.

Initial Pressure, 2 atmospheres absolute.
Initial Temperature, 17° C.

| Per cent. Gas (97·5 per cent. pure). | Flame Velocity. cm./sec. | Max. Press. Time. secs. | Max. Pressure. lb./sq. in. abs. | Pressure Ratio. |
|--------------------------------------------|-----------------------------|-------------------------------|------------------------------------|--------------------|
| 17 | 26·6 | ∞ | ∞ | ∞ |
| 20 | 50·7 | ·80 | 169·5 | 5·77 |
| 25 | 84·1 | ·385 | 209 | 7·12 |
| 30 | 107 | ·231 | 231·5 | 7·86 |
| 35 | 139 | ·211 | 240 | 8·16 |
| 40 | 145 | ·175 | 243 | 8·27 |
| 45 | 137 | ·170 | 242·5 | 8·25 |
| 50 | 129 | ·189 | 224·5 | 7·65 |
| 55 | 101 | ·251 | 208·5 | 7·10 |
| 60 | 77·5 | ·390 | 178 | 6·05 |
| 65 | ∞ | ·920 | 143 | 4·87 |

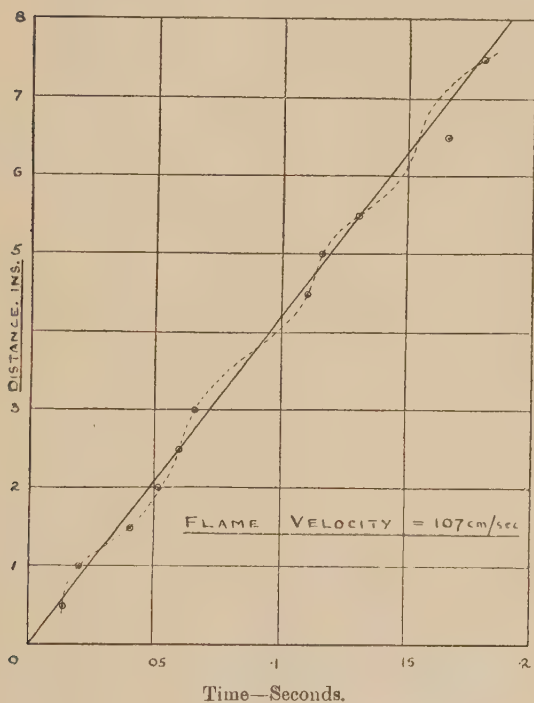
complete to give consistent results. Plotted out as Time-distance ordinates for each plug the points were rather erratic, and on repetition were not constant. By repeating each point two or three times, and carrying out two such experiments, one at one atmosphere initial, another at two, some idea of the manner in which the flame spread could be obtained. There appear to be four main effects resulting from incomplete diffusion: (1) The Velocity varies along different radial lines; (2) There is an accelerated motion after about one-half of the distance is travelled; (3) The mean velocity is lower than for complete diffusion; (4) The time of combustion is increased. With the exception of (2) these might have been predicted beforehand. It would seem that the acceleration must be due to the increase of homogeneity resulting from the adiabatic compression of the unburnt portion of the mixture. The decrease in the mean velocity is quite considerable. For a 25 per cent. gas mixture, the mean flame velocity was 48·9 cm./sec. When completely diffused the constant velocity is 97·7 cm./sec. The corresponding times of combustion—*i.e.*, the times to attain the maximum pressure—are ·416 sec. and ·280 sec.

Fig. 1 gives a velocity curve which is typical of all the curves obtained for any Air/Gas ratio and any initial pressure, and in which diffusion is complete. A mean straight line can be put through the points. This uniform velocity is one of the chief results that these investigations have yielded. It has usually been assumed that when a mixture is exploded in a closed vessel there will be an accelerated motion. Several reasons have been advanced in support of this:—(1) The rise in temperature produced by the combustion of the portion first inflamed will cause an

expansion, and this will have the effect of projecting the flame front forward at an increasing velocity. (2) As the flame advances the unburnt portion is compressed, thus bringing it nearer the ignition temperature. Less heat will therefore be required from the burning zone to influence it. (3) The increase of pressure, quite apart from the rise in

Fig. 1.

Mixture—30 per cent. Gas, 70 per cent. Air.
Initial Pressure—2 Atmos.



temperature, will increase the speed of combustion. (4) Also, if we look on flame-propagation from a point of view of conduction of heat, there will be an increase in the temperature difference between burning and unburnt zones due to the compression of the total change.

It is now known that (3) is not an accelerating but a decelerating influence in the case of carbon monoxide and air. This will be referred to later.

It has yet to be shown that flame spreads with a constant velocity in any other than carbon monoxide mixtures. In the case of hydrogen, Nagel has shown that an increase of initial pressure results in a lower time of combustion, and therefore presumably in a higher flame velocity. The flame speed in hydrogen therefore might possibly be accelerated. The difference in the detonating properties of these two gases is also well known, and it would seem quite likely that this depends to a large extent on the possibility of an accelerated flame motion and therefore of the behaviour of the gases when exploded under different pressures. No experiments have been done on hydrogen as yet, and it is rather doubtful if records will be obtained with the present apparatus. The slower combustion of carbon monoxide at higher pressures is the only fact that will explain a constant velocity, and it must be inferred that, since all the forces operating are interdependent—that is, they all depend on changes of pressure,—they can only be developed to such an extent that they will always counterbalance.

It will be seen from fig. 1 that a wavy line can be put through the actual points. This is not due to experimental errors, as these are much smaller than the observed discrepancies. It was thought at first that the plugs might be so disposed that the effects of convection would produce these differences from the mean velocity. Some experiments were done to find out how the flame front is distorted by convection currents, and from these it is fairly certain that in the upper hemisphere the flame front is truly spherical. Below the centre line there is a flattening out of the flame even at velocities of over 100 cm./sec. Most of the plugs are in the upper half, and only one plug in the lower half would show this lag. There is little doubt now that the wave is a true oscillation of the flame front. This oscillation is always present with any mixture and any initial pressure, the frequency being fairly constant and the amplitude, except when much higher temperatures are recorded, is also constant.

If resonance of the whole mass is set up, analogous to that found in tube experiments, the frequency of the vibrations would be higher (Mason & Wheeler, Chem. Soc. Trans. 1919). The initial oscillation must be started by the pressure waves that are being sent out both through the burning core and to the walls. Those will be reflected and cross and re-cross at the flame front. The speed of those through the burning mass will be much higher than those through the unburnt part, and it may be assumed that the actual

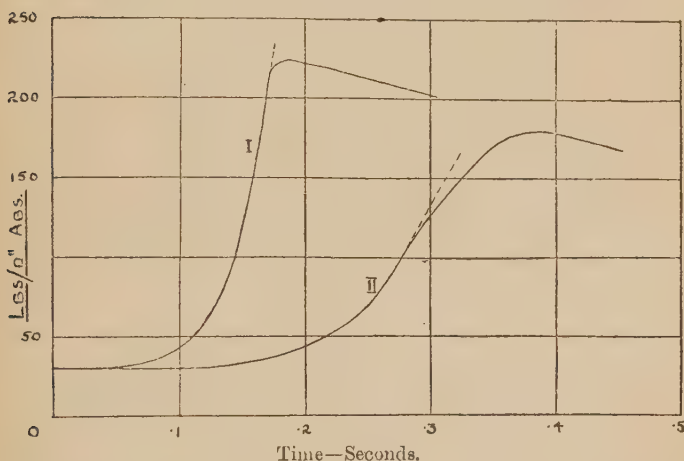
frequency of the flame is the resultant of these two vibrations.

An interesting point about all the pressure records obtained, two of which are reproduced in fig. 2, is that the flame velocity may be obtained approximately from them. With carbon monoxide-air mixtures, in no case is the combustion of the whole mass complete when the flame has reached the walls. During the subsequent combustion cooling is taking place, and the time when this begins is shown by a point of inflexion on the pressure curve. This has been used later in an estimation of cooling losses.

Fig. 2.

Pressure Records— I. 50 per cent. Gas, 50 per cent. Air.

II. 60 per cent. Gas, 40 per cent. Air.

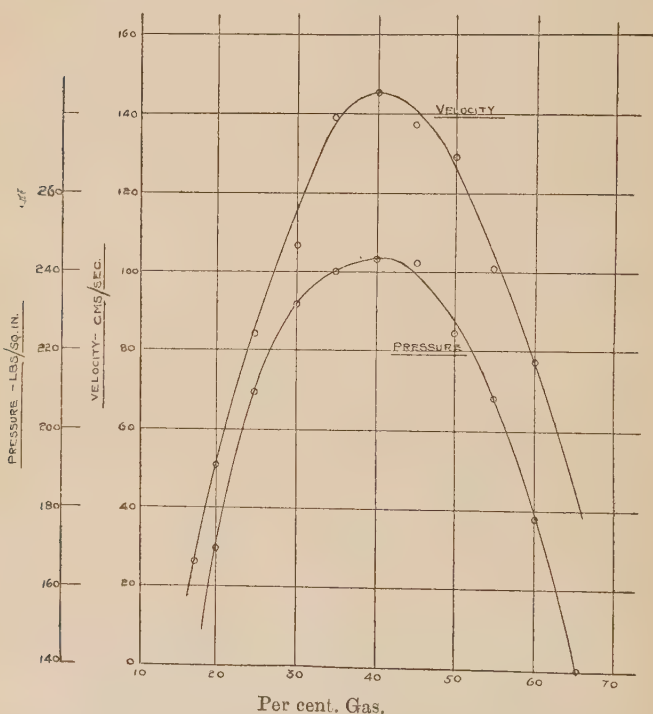


In Table I. are given the results of a series of experiments with different mixture strengths. The flame velocity and maximum pressure are plotted in fig. 3. The peaks of both curves occur at about 40 per cent., the theoretical mixture is 30 per cent. As far as the velocity is concerned, this is in agreement with practically all determinations of flame-propagation, whatever the conditions. Unfortunately, very few experiments have been done on propagation in a tube with carbon monoxide. With methane and hydrogen the shift of the peak of the curve from the theoretical mixture might be explained simply by a theory of conductivity, the thermal conductivity of both of these gases being greater than air.

The conductivity of carbon monoxide, however, is about the same as that of air.

Considering the pressure curve, Tizard and Pye (Proc. Auto. Eng. 1920) have shown that the phenomenon of the maximum pressure occurring with a rich mixture may be accounted for by the dissociation of the products of combustion. This occurs because the percentage of excess carbon monoxide is increasing, and this has a powerful effect in limiting the amount of dissociation that can occur.

Fig. 3.



It would seem at the outset, then, that the velocity of the flame is mainly a function of flame temperature, and that the position of the peak of this curve is also determined by the amount of dissociation.

If we accept some theory of conduction, then flame speed will depend on the ignition temperature of the mixture as well as on flame temperature and conductivity. This

ignition temperature, however, probably plays a very small part indeed, if any, in determining the velocity of flame-propagation. In some later experiments where the rise of temperature, due to adiabatic compression, of the unburnt mixture is much higher, because there is less subsequent combustion, there is still no sign of an accelerated motion which might be expected if flame velocity were determined by the rate at which one layer immediately in front of the flame can be raised to the ignition temperature.

It is difficult also to explain how a detonation wave can travel through a mixture which has not been previously compressed up to the ignition temperature, as it does in an open-ended tube. Any conduction theory of propagation appears therefore to be quite untenable.

There is a distinction between the rate of combustion and the rate of propagation of combustion, although the two must be closely related, and at the flame front itself precisely the same process must be going on that is going on in the flame zone. If, then, we neglect altogether the time required to raise a layer up to the ignition temperature, we should expect that the velocity of the flame would be determined by the same factors that determine the rate of combustion—that is, flame temperature and the mass factor. If this is so,

$$V = KC_1^2C_2,$$

where $\log K = A + BT$ (Nernst) and C_1 , C_2 are the concentrations of carbon monoxide and oxygen.

As the peaks of the two curves of pressure (and therefore temperature) and velocity are practically at the same mixture, the value of the K would be such that the temperature factor overwhelms the mass factor. The latter alone would give a maximum at 66 per cent. This does, however, operate in the right direction, as is seen if we take a horizontal line on the Velocity Curve. For the same flame velocity the temperature of the stronger mixture is lower than that of the weaker.

In the preliminary experiments attempts were made to obtain more than one velocity determination for each explosion by using two recording plugs at different distances from the centre, each in series with its own external gap. By suitable adjustment of the electrical conditions two records could be obtained with fair regularity, but on examination it was found that the second record did not give the velocity but the arc struck invariably some time

after the flame had passed through the plug-points. In addition, there was no consistent time-lag. On examining a number of records it was found that the first plug determined the striking of the arc at the second—that is, the first arc ceased and the second commenced at a constant time from striking for a particular first plug, irrespective of the particular second plug used. It was thought that when a certain phase in the combustion was reached at the first gap, the tendency to arc at the second overcame the effect at the first. This was tried outside the sphere, using two plugs and two bunsen flames, but in most cases it gave the condition for the velocity at the second plug. It had previously been found that no reliance could be placed on bunsen experiments outside the sphere. The conditions are very different. Since, however, the presence of the second plug did not affect the velocity determination at the first, two plugs were used throughout the greater part of the experimental work.

All results using any mixtures of CO and air gave similar results, and on analysis it was found that the particular phase of combustion recorded at the wall of the sphere occurred in most cases just after the attainment of maximum pressure. That is to say, the records indicate the approach to complete combustion when there is a great diminution of chemical activity. It is realised that complete combustion can only be approached asymptotically, and, in fact, using large resistances in series, arcs have been produced which show this tailing off effect.

That combustion is certainly taking place after the flame reaches the wall is shown by the pressure results—that is, the rise in pressure beyond the point of inflexion. Hopkinson (*Proc. Roy. Soc.* 1906), using coal gas, observed that the flame filled the vessel before maximum pressure. Wheeler (*Trans. Chem. Soc.* 1918), using methane, found that the flame filled the vessel at the time of maximum pressure, but his pressure records are not above criticism. Hopkinson explains his subsequent pressure rise by the fact that a hot core is produced at first which must equalise through the vessel, the change in specific heats giving the additional pressure rise. If this is the case in some of the present faster-burning mixtures which approach Hopkinson's velocities, there should be less rise in the slower burning mixture owing to greater time available for temperature equalisation. The reverse is invariably the case, and the only possible explanation is prolonged combustion. From this can be generalised that

combustion does not take place instantaneously at any spherical shell using carbon monoxide and air, and probably does not do so with any other gas, although in some cases it approaches instantaneous combustion—*e. g.*, hydrogen and oxygen.

In all mixtures of CO and air, it was found that combustion was nearing equilibrium at the centre as the flame strikes the wall. This, of course, probably only holds for this size of sphere. A curve can be plotted showing the time of combustion at any spherical shell against the radius of the shell. A parabolic curve is produced, giving a maximum time for most mixtures at a radius of $2\frac{1}{2}$ inches, minimum at the wall, excluding of course a very thin layer in contact with the cold wall, and at the centre a time midway between the maximum and minimum.

By assuming a uniform rate of heat addition in any spherical shell, together with the time of combustion and the flame velocity, the proportion of total heat evolved can be calculated for any instant after sparking the mixture. A simple integration gives the proportion of heat addition for the whole sphere. Assuming constant specific heat, the rise in pressure is proportional to the actual heat evolved. Plotting heat evolved against time, it was found that the theoretical heat evolved was considerably less than the actual. With variable specific heats, the actual heat curve should be higher still. This indicates that heat addition in a spherical shell takes place more rapidly at first and then at an ever-diminishing rate. Presuming combustion to follow the law of mass action, the mass factor rapidly counteracts the temperature coefficient, giving an asymptotic approach to chemical equilibrium.

In making temperature calculations for gaseous explosions, certain assumptions have to be made and certain data used. The principal assumption made in these calculations is that chemical equilibrium is nearly reached at the time of maximum pressure, and the only "after-burning" that takes place is the recombination of dissociated products. In all cases the peak of the curve is reached when the rate of heat addition equals the rate of cooling. From the slopes of the pressure curve just before and after the peak there must be a very sudden change, which cannot be satisfactorily explained by the "after-burning" theory. This, however, would be the result expected if chemical equilibrium were reached.

At these high temperatures very little reliable information is available for volumetric heats and equilibrium constants

for dissociation. On examination of the existing data, the following results of Pier and Bjerrum have been thought most reliable :—

Vol. ht. Nitrogen.. $4.9 + .45 \times 10^{-3}t$.

Carbon Dioxide .. $6.8 + 3.3 \times 10^{-3}t - .95 \times 10^{-6}t^2 + .1 \times 10^{-9}t^3$

being the mean vol. hts. between 18°C . and $t^\circ\text{C}$.

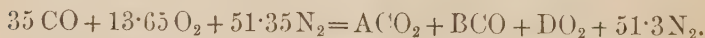
For the equilibrium constants for CO_2 $K = \frac{P_{\text{CO}}^2 \times P_{\text{O}_2}}{P_{\text{CO}_2}^2}$

$$2000\text{--}2500 \text{ abs. } \log K = 9.41 - \frac{29500}{T \text{ (abs.)}}$$

$$2500\text{--}3000 \text{ abs. } \log K = 9.57 - \frac{29920}{T}$$

For the calculation of the mean temperature from the pressure, a knowledge of the contraction factor is necessary. This depends upon the degree of dissociation, which in turn depends upon temperature and pressure. In the experimental work, from different explosions of similar mixtures under similar conditions, slightly varying maximum pressures were obtained. The variation in maximum pressure was sometimes as much as 2 per cent. from the mean value, with the variation of time to reach maximum pressure somewhat greater. These discrepancies cannot be wholly explained by variations in mixture strength, as great care was taken over this to ensure results being as uniform as possible. Similar phenomena were observed by Bjerrum (*Zeit. Phys. Chem.* 1912) in his CO experiments, but with no other gases. Mean values have always been taken and results for different mixtures plotted, and the values used in the calculations taken from the mean curve. This method was adopted for all experimental results, so that errors would not be magnified in calculation.

To determine the contraction factor, the chemical equation at equilibrium must be derived. Take a mixture of 35 per cent. CO, 65 per cent. Air, and consider 100 vols of mixture before explosion :



We have immediately $A + B = 35$ and $2A + B + 2D = 62.3$.

The third equation is derived from the formula for K and the gas law :

$$K = \frac{B^2 D P_0 T_e}{A 100 T_0} \quad (P_0 \text{ is initial press. in atmos. absolute}).$$

Choose a value for T_e the maximum temperature, and solve the equations by trial and error. The contraction factor is thus determined and the final temperature calculated, which must agree closely with the assumed temperature. It was found that, with mixtures of 45 per cent. gas and upwards, the dissociation was negligible and the contraction factor determined immediately.

TABLE II.

Initial Pressure, 2 atmospheres absolute.
Initial Temperature, 290° absolute.

| Per cent. CO (pure). | Max. Temp. | Corrected Temp. | Per cent. Cooling loss. |
|-------------------------|------------|--------------------|----------------------------|
| 20 | 1890 abs. | 2305 abs. | 25.9 |
| 25 | 2388 | 2544 | 10.95 |
| 30 | 2633 | 2692 | 5.35 |
| 35 | 2715 | 2757 | 4.20 |
| 40 | 2724 | 2772 | 3.29 |
| 45 | 2634 | 2695 | 2.71 |
| 49 | 2485 | 2543 | 3.02 |
| 53 | 2310 | 2395 | 4.71 |
| 58 | 1990 | 2150 | 9.89 |
| 62 | 1670 | 1976 | 20.55 |

In estimating the cooling correction it has been assumed that the heat lost by radiation up to the time of maximum pressure is small compared with the heat lost by conduction. According to David (Phil. Trans. 1912), this is justifiable in a silvered vessel. Then the actual heat lost to the walls should equal a constant times the product of temperature difference from flame to wall, and the time flame is in contact with the wall up to the maximum pressure. Considering any pressure curve, there is a bend over from the time the flame strikes the wall. If the walls were impervious to heat, the curve would have continued up. Similarly, the cooling curve may be produced back, and the intersection should give approximately the theoretical pressure. By this means the constant can be calculated for any particular mixture. It must be noted that this method is only applicable when dissociation is negligible, as in other cases the pressure curve does not show a true heat addition or cooling curve. Four such mixtures were available, 45 per cent., 50 per cent., 55 per cent., and 60 per cent. gas (97 per cent. purity). The actual and theoretical pressures and temperatures were obtained as already explained. Using Pier's values for the volumetric heats the heat evolved per grm. molecule is known, and the difference between the energies at these two

temperatures is the heat loss to the wall. The time in seconds is known from the pressure curve and flame velocity, and the constant can be calculated. The maximum variation for these results was 10 per cent. about a mean value of 7.41. In view of the errors involved in producing the curves and the great differences in heat loss for the curves, this variation is quite good, and the mean constant was used for correcting all temperatures, the actual correction being the reverse process of the above. This reversal tends to eliminate any errors in Pier's results used.

The correction of mixtures which dissociate is rather complicated. The total heat evolved per gm. mol. is calculated as before, being the sum of the pressure energy and cooling loss. If there were no cooling this extra heat would not all appear as additional pressure energy, since more of the products would be dissociated at the higher temperature. The percentage of CO_2 formed at the lower temperature has already been calculated in determining this temperature. (Coefficient A in equilibrium equation.) By assuming the higher theoretical temperature, a new percentage of CO_2 is calculated, less than the previous one. The total heat evolved is then diminished in the ratio of these two percentages, and this heat used to calculate the theoretical temperature which must agree with that assumed. The extent of this correction can be seen in the case of the 30 per cent. mixture. The mean temperature calculated as above 2692° abs. If no allowance had been made for change of dissociation, the temperature would have been 2750° abs.

The cooling loss expressed as a percentage is the ratio of the heat loss to the wall to the total heat evolved by the gas up to the maximum pressure, after the temperature is lowered by cooling, and is given in Table II. It is remarkable that the percentage should vary so greatly for different mixtures of the same gases, being least for a rich mixture.

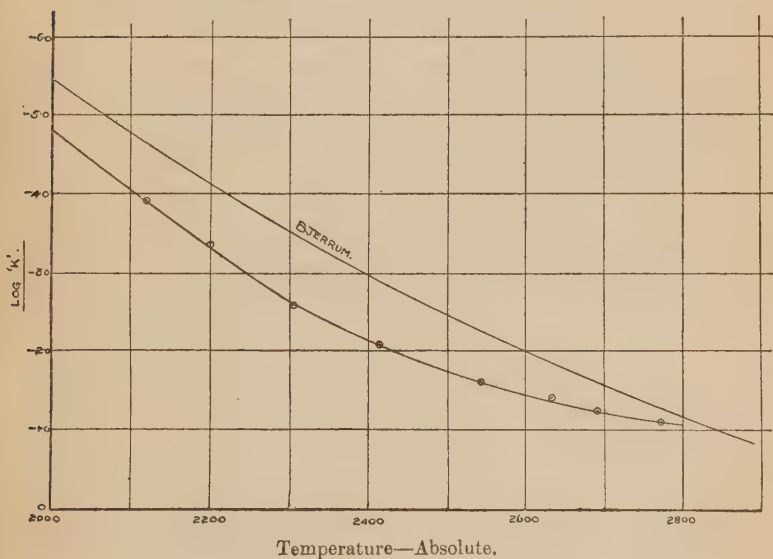
Sufficient information is now available for checking Pier's figures for volumetric heats, although the values for the different constituents cannot yet be separated. In order to eliminate any errors in dissociation, it is advisable to consider, as Pier did, only the maximum temperatures for rich mixtures, in which dissociation is negligible. In this case, it is found that the temperatures fall on a straight line, although no significance is attached to this at present. The calorific value for CO is taken at 68 kg.cals./gm. molecule, and from the proportion of CO_2 in the exhaust products the total heat of the exhaust is calculated, from which the mean volumetric heat is easily determined. At the higher temperatures,

about 2700 abs., the agreement with Pier's values is very close, but for the lower temperatures the present results are higher than those of Pier. At 2066 abs. the values are 6.92 and 6.32 respectively for 60 per cent. CO mixture, while at 2713 the values are 7.32 and 7.21. This agreement of Pier's figures at very high temperatures was found by Bjerrum.

The amount of dissociation can also be calculated from the temperature curve, since two mixtures which give the same temperature must have the same percentage of carbon dioxide at equilibrium. On the rich side this composition is

Fig. 4.

Variation of Equilibrium constants with Temperature.



known, and hence for any dissociated mixture the amount of CO_2 formed can be calculated. The values of the equilibrium constants are then determined by the formula given. The values are shown plotted against those of Bjerrum in fig. 4. In correcting for cooling, Bjerrum makes no mention of the change in dissociation, so he presumably neglected this. If it is neglected in the present results, a curve is produced which agrees very closely with that of Bjerrum. The temperatures have all been worked out using Bjerrum's values, but, since the correction will only affect the contraction in volume, the temperatures will not be altered appreciably.

TABLE III.

Mixtures of Gas and Air at varying initial pressures.

| CO per cent. (97.5 per cent. pure). Per cent. | Initial Press. lb./sq. in. abs. | Velocity. cm./sec. | Final Press. lb./sq. in. abs. | Press. Time. secs. | Press. Ratio. |
|--------------------------------------------------------|------------------------------------------|-----------------------|----------------------------------------|-----------------------|------------------|
| 25 | 14.7 | 97.7 | 94 | .280 | 6.39 |
| 25 | 29.4 | 84.1 | 209.5 | .385 | 7.12 |
| 25 | 44.1 | 69.7 | 313.5 | .482 | 7.10 |
| 25 | 58.8 | 59.7 | 425 | .550 | 7.22 |
| 25 | 73.5 | 49.0 | 543 | .668 | 7.39 |
| 25 | 88.2 | 42.2 | 638 | .990 | 7.24 |
| 25 | 102.9 | 37.2 | 768 | 1.01 | 7.47 |
| 30 | 29.4 | 107 | 231.5 | .231 | 7.86 |
| 30 | 58.8 | 90.3 | 486 | .335 | 8.25 |
| 30 | 88.2 | 76.4 | 780 | .560 | 8.85 |

The effect of initial pressure on a mixture of CO and air is to greatly reduce the flame velocity and increase the time to reach maximum pressure. This is more pronounced in the case of the weaker mixtures. In addition at the higher pressures difficulties were experienced in exploding the mixtures, and in order to obtain records the gaps of the recording plugs in the sphere were decreased from 7 mm. at 1 atmosphere to $1\frac{1}{2}$ mm. at 7 atmospheres. Bone (Proc. Roy. Soc. 1923-24) found a similar difficulty in exploding his mixtures at 50 atmospheres, and resorted to the fusing of a wire. Nagel carried out experiments with hydrogen and found a decrease in the time of combustion with increase in initial pressure, while some investigators using coal gas found an increase in combustion time, others found a decrease. The present results offer an explanation of the latter discrepancy, since the variation in flame velocity will doubtless depend upon the relative percentages of hydrogen and carbon monoxide in the coal gas. This emphasises the need for working with pure gases until these phenomena are understood.

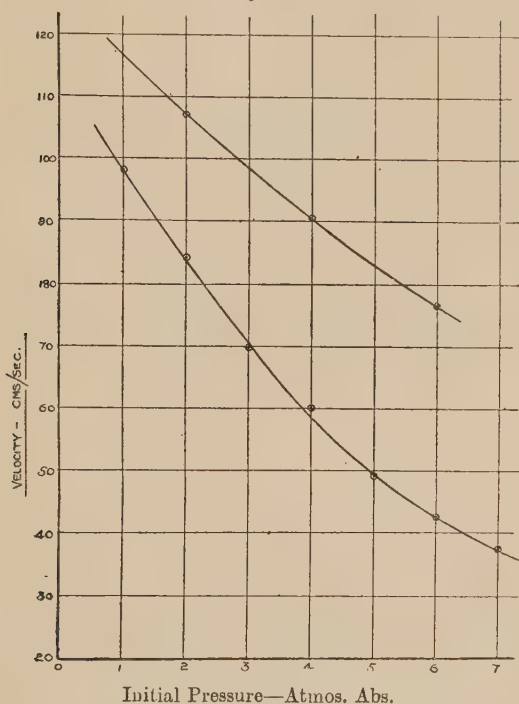
This research confirms the work of others, that the lower limit of inflammability of CO and air is raised with increase of initial pressure. This does not explain why the velocity is lowered, but merely shifts the question. Bone attempts to explain his high-pressure work by an energy-absorbing property of nitrogen. In some later experiments he asserts that this is negligible below 10 atmospheres initial pressure, and so cannot account for the present reduction.

Since the velocity of hydrogen increases slightly, while that of CO decreases considerably, the explanation must be

sought in the different chemical reaction. It is well known that for the combustion of CO the presence of water vapour is necessary, which is dissociated, the nascent oxygen oxidizing the CO. Thus the whole reaction may depend upon the rate of dissociation of water vapour. The law of mass action for a tri-molecular reaction shows that the percentage of oxygen dissociated will be roughly inversely

Fig. 5.

Variation of Velocity with Initial Pressure.



proportional to the cube root of the absolute pressure. This rough agreement is found to exist between the pressure and flame velocity. This cannot be examined rigidly, as factors enter which cannot be definitely determined, but the explanation is put forward as a possible solution.

Experiments have been carried out with mixtures of CO_2 , O_2 , and N_2 at 2 atmospheres initial pressure, keeping the ratio of CO/O_2 constant at 1.97 to 1 and steadily decreasing the nitrogen content. At first the increase in velocity is

proportional to the decrease in nitrogen, but afterwards the change in velocity becomes smaller and smaller. The results, on the whole, are very erratic. As the flame velocity increases, the oscillation of the flame front becomes very violent and of large amplitude. It is obvious for this particular size vessel that a point to point method is not suitable for velocity determinations above 200 cm./sec. Results, however, have been obtained by plotting from a large number of experiments and drawing a mean line. The following results serve to show the velocity increase:—

| | |
|-----------------------------------|---------------------------|
| N ₂ ... 56.5 per cent. | Velocity ... 107 cm./sec. |
| 42 " | 199 " |
| 0 " | approx. 350 " |

It is quite probable that when hydrogen is exploded in this vessel the same phenomenon will occur.

In addition, variations in maximum pressure and also time to reach maximum pressure occurred, both variations being in excess of likely errors in gas composition or water content.

As the nitrogen content is decreased, the time of combustion of an individual spherical shell also decreases, as determined by the two-point method previously explained. This became small enough to permit of two velocity determinations—that is, combustion had sufficiently decreased at the first gap before the flame struck the second. Ultimately, this could be obtained with two consecutive plugs whose radial distances differed by half an inch. In this case, with sufficient external gaps it would have been possible to have taken a complete velocity record at one explosion. Time, however, did not permit an attempt. As a confirmation of this, the point of inflexion disappeared from the pressure curve, which continued up to a sharp point when cooling set in. This sharp point also supports the assumption of an approach to chemical equilibrium as opposed to after-burning, apart from recombustion of dissociated products. This refers, of course, to a perfectly homogeneous mixture.

The following are the principal conclusions regarding the combustion of carbon monoxide at constant volume:—

- (1) Flame velocity is at all times uniform, and in addition there is a regular vibratory motion at the flame front.
- (2) Combustion is not complete when the flame strikes the wall of the explosion vessel. Instantaneous heat addition at any point can be approached under certain conditions, but probably never attained.

- (3) Convection currents do not play a very important part, even in the weaker mixtures.
- (4) The maximum velocity, pressure, and temperature occur with a rich mixture containing about 40 per cent. CO. The phenomena can be explained by dissociation.
- (5) The percentage cooling loss is a minimum with a mixture of 45 per cent. CO and greatly increases as the upper and lower limits are approached.
- (6) Pier's values for volumetric heats and Bjerrum's dissociation are slightly lower than values determined in this research.
- (7) An increase of initial pressure greatly decreases the inflammability of CO and air.
- (8) The effect of adding inert gas is to cause a slower flame velocity and a slower subsequent combustion.

For a fuller description of the foregoing research and details of calculations, etc., reference can be made to the original theses of the authors at the Birmingham University.

In conclusion, the two collaborators wish to express their thanks to Professor Burstall at the Mechanical Engineering Department of the University for his encouragement during the prosecution of this research.

CXIII. *The Whirling Speeds of Shafts carrying Concentrated Masses.* By R. C. J. HOWLAND, M.A., M.Sc., University College, London*.

1. Preliminary.

THE whirling speeds of shafts carrying loads whose moments of inertia are negligible were considered by Dunkerley†, who gave a rule for computing the first whirling speed. His method consisted in finding the whirling speed for the case when all the loads but one were removed, and adding the squared reciprocals of the separate speeds found in this way. The sum was stated as the squared reciprocal of the whirling speed when all the loads were carried simultaneously. This rule, which was found to give approximately correct results in a number of cases, was without theoretical foundation, and its accuracy could be estimated only by experiment.

* Communicated by Prof. L. N. G. Filon, M.A., D.Sc., F.R.S.

† Phil. Trans. A, clxxxv. (1894).

In a recent paper, Prof. H. H. Jeffcott* has given a theoretical derivation of Dunkerley's rule, by a method which enables all the whirling speeds of the loaded shaft to be computed to any desired degree of accuracy. The same method has been used by Hahn†.

The present paper attacks the problem from a different standpoint. Dunkerley's rule is arrived at by a theoretical method, which gives at the same time a correction term. A numerical estimate of the error involved in using the rule is made. The application of the method to non-uniform shafts is also considered.

{2. General Method of Computing Whirling Speeds.

In the usual notation, the equation giving the deflexion of the shaft due to its rotation is

$$\frac{d^2}{dx^2} \left(EI \frac{d^2 y}{dx^2} \right) = m \omega^2 y, \quad . \quad . \quad . \quad . \quad (1)$$

where EI and m may both be functions of x . The discussion is a little simplified by writing the equation in its non-dimensional form. This is achieved by means of the substitutions,

$$\left. \begin{aligned} x &= lx', \\ y &= ly', \\ m &= \rho_0 A_0 f(x'), \\ EI &= E_0 I_0 \phi(x'), \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad (2)$$

where l is the length of the shaft, and ρ_0 , A_0 , E_0 , I_0 give the density, sectional area, elastic modulus, and second moment of section at some chosen point of the shaft. In what follows, they will be taken as referring to the end, $x=0$. If these substitutions are made, and the dashes then dropped, equation (1) is replaced by

$$\frac{d^2}{dx^2} \left(\phi(x) \frac{d^2 y}{dx^2} \right) = \theta^4 f(x) y, \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\theta^4 = \frac{\rho_0 A_0 \omega^2 l^4}{E_0 I_0} . \quad . \quad . \quad . \quad . \quad (4)$$

* R. S. Proc. A, xciv. (1918).

† "Note sur la Vitesse Critique des Arbres et la Formule de Dunkerley," E. Hahn, *Schweizerische Bauzeitung*, Nov. 1918.

The whirling speeds are given by the critical values of θ^4 for which (3), together with the end conditions, give a value for y other than zero.

A method of solving equation (3) in powers of θ^4 was suggested by Messrs. Cowley and Levy *. It consists simply in assuming an expansion of this type and substituting in the equation. Equating powers of θ on the two sides results in a series of equations from which the coefficients may be found by integration.

Assume, then, that

$$y = y_0 + \theta^4 y_1 + \theta^8 y_2 + \dots, \quad \dots \quad (5)$$

where $y_0, y_1, y_2 \dots$ are functions of x . Then we have at once from (3)

$$\left. \begin{aligned} \frac{d^2}{dx^2} \left(\phi(x) \frac{d^2 y_0}{dx^2} \right) &= 0, \\ \frac{d^2}{dx^2} \left(\phi(x) \frac{d^2 y_r}{dx^2} \right) &= f(x) y_{r-1}, \end{aligned} \right\} \quad \dots \quad (6)$$

from which $y_0, y_1 \dots$ can be found successively by integration.

If the shaft is uniform, but carries masses which do not affect its elastic properties, $\phi(x)$ will be unity everywhere. The equations then reduce to

$$\left. \begin{aligned} \frac{d^4 y_0}{dx^2} &= 0, \\ \frac{d^4 y_r}{dx^2} &= f(x) y_{r-1}, \end{aligned} \right\} \quad \dots \quad (7)$$

and their solution is

$$\begin{aligned} y_0 &= A + Bx + Cx^2 + Dx^3, \\ y_1 &= A \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \\ &\quad + B \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x f(x) dx \\ &\quad + C \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^2 f(x) dx \\ &\quad + D \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x) dx, \end{aligned}$$

and so on ;

* "On a Method of Analysis suitable for the Differential Equations of Mathematical Physics," *Phil. Mag.* xli. April 1921.

or

$$y = Af_1(x) + Bf_2(x) + Cf_3(x) + Df_4(x), \quad \dots \quad (8)$$

where

$$\left. \begin{aligned} f_1(x) &= 1 + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \\ &\quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \\ &\quad + \text{etc.} \\ f_2(x) &= x + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x xf(x) dx \\ &\quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x xf(x) dx \\ &\quad + \text{etc.} \\ f_3(x) &= x^2 + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^2 f(x) dx \\ &\quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^2 f(x) dx \\ &\quad + \text{etc.} \\ f_4(x) &= x^3 + \theta^4 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x) dx \\ &\quad + \theta^8 \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x f(x) dx \int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x) dx \\ &\quad + \text{etc.} \end{aligned} \right\} \quad \dots \quad (9)$$

Consider now a shaft with a short bearing at each end. Then

$$y = \frac{d^2 y}{dx^2} = 0$$

when $x=0$ or 1 . Substituting these values in (8) and using the obvious relations,

$$\begin{aligned} f_1(0) &= 1, & f_2(0) &= f_3(0) = f_4(0) = 0, \\ f_1''(0) &= f_2''(0) = f_4''(0) = 0, & f_3''(0) &= 2, \end{aligned}$$

we have

$$A = C = 0$$

and

$$f_2(1)f_4''(1) = f_2''(1)f_4(1). \quad \dots \quad (10)$$

Similar equations may be found corresponding to other end conditions.

3. Derivation of Dunkerley's Rule.

When the shaft carries no additional masses, $f(x)$ reduces to unity at all points. The exact solution of (3) for this case is known, and the accuracy of the present method can be tested. In the series of equations (9) the coefficients are seen, in this case, to decrease with great rapidity, and this suggests that the lowest value of θ may be obtained approximately by neglecting all the powers of θ^4 . The effect of including only the first two terms of the series in the case of a shaft carrying concentrated masses will now be examined.

Let the shaft have attached masses M_1, M_2, \dots at distances a_1l, a_2l, \dots from $x=0$; we then have $f(x)=1$ except for $x=a_1, a_2$, etc., while at these points

$$\lim_{\epsilon \rightarrow 0} \int_{a_r - \epsilon}^{a_r + \epsilon} f(x) dx = \frac{M_r}{\rho A l} = \mu_r. \quad (11)$$

Hence the required integrals are as follows:—

| | $x > a_1.$ | $x > a_2.$ | |
|------------------------------------------------------------|---------------------|-----------------------------------------|------------------------------------------------|
| $\int_0^x x f(x) dx$ | $= \frac{1}{2} x^2$ | $+ \mu_1 a_1$ | $+ \mu_2 a_2$ + etc. |
| $\int_0^x dx \int_0^x x f(x) dx$ | $= \frac{1}{3} x^3$ | $+ \mu_1 a_1 (x - a_1)$ | $+ \mu_2 a_2 (x - a_2)$ + etc. |
| $\int_0^x dx \int_0^x dx \int_0^x x f(x) dx$ | $= \frac{1}{4} x^4$ | $+ \frac{1}{2} \mu_1 a_1 (x - a_1)^2$ | $+ \frac{1}{2} \mu_2 a_2 (x - a_2)^2$ + etc. |
| $\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x f(x) dx$ | $= \frac{1}{5} x^5$ | $+ \frac{1}{6} \mu_1 a_1 (x - a_1)^3$ | $+ \frac{1}{6} \mu_2 a_2 (x - a_2)^3$ + etc. |
| $\int_0^x x^2 f(x) dx$ | $= \frac{x^4}{4}$ | $+ \mu_1 a_1^3$ | $+ \mu_2 a_2^3$ + etc. |
| $\int_0^x dx \int_0^x f(x) x^3 dx$ | $= \frac{x^5}{20}$ | $+ \mu_1 a_1^3 (x - a_1)$ | $+ \mu_2 a_2^3 (x - a_2)$ + etc. |
| $\int_0^x dx \int_0^x dx \int_0^x x^3 f(x) dx$ | $= \frac{x^6}{120}$ | $+ \frac{1}{2} \mu_1 a_1^3 (x - a_1)^2$ | $+ \frac{1}{2} \mu_2 a_2^3 (x - a_2)^2$ + etc. |
| $\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x) dx$ | $= \frac{6x^7}{7}$ | $+ \frac{1}{6} \mu_1 a_1^3 (x - a_1)^3$ | $+ \frac{1}{6} \mu_2 a_2^3 (x - a_2)^3$ + etc. |

Hence

$$\left. \begin{aligned} \int_0^1 dx \int_0^x x f(x) dx &= \frac{1}{6} + \sum_{r=1}^n \mu_r a_r b_r, \\ \int_0^1 dx \int_0^x dx \int_0^x \int_0^x x f(x) dx &= \frac{1}{15} + \frac{1}{6} \sum_{r=1}^n \mu_r a_r b_r^3, \\ \int_0^1 dx \int_0^x x^3 f(x) dx &= \frac{1}{20} + \sum_{r=1}^n \mu_r a_r^3 b_r, \\ \int_0^1 dx \int_0^x dx \int_0^x \int_0^x x^3 f(x) dx &= \frac{6}{7} + \frac{1}{6} \sum_{r=1}^n \mu_r a_r^3 b_r^3, \end{aligned} \right\} \quad (12)$$

where $b_r = 1 - a_r$.

If terms in θ^8 are neglected, we therefore have

$$\left. \begin{aligned} f_2(1) &= 1 + \theta^4 \left[\frac{1}{15} + \frac{1}{6} \sum_{r=1}^n \mu_r a_r b_r^3 \right], \\ f_2''(1) &= \theta^4 \left[\frac{1}{6} + \sum_{r=1}^n \mu_r a_r b_r \right], \\ f_4(1) &= 1 + \theta^4 \left[\frac{6}{7} + \frac{1}{6} \sum_{r=1}^n \mu_r a_r^3 b_r^3 \right], \\ f_4''(1) &= 6 + \theta^4 \left[\frac{1}{20} + \sum_{r=1}^n \mu_r a_r^3 b_r \right]. \end{aligned} \right\} \quad \dots \quad (13)$$

Substituting these values in (10) and again neglecting a term in θ^8 ,

$$\begin{aligned} 6 + \theta^4 \left[\frac{1}{10} + \sum_{r=1}^n \mu_r (a_r^3 b_r + a_r b_r^3) \right] \\ = \theta^4 \left[\frac{1}{6} + \sum_{r=1}^n \mu_r a_r b_r \right], \end{aligned}$$

$$\begin{aligned} \text{or} \quad 6 &= \theta^4 \left[\frac{1}{15} + \sum_{r=1}^n \mu_r a_r b_r (1 - a_r^2 - b_r^2) \right] \\ &= \theta^4 \left[\frac{1}{15} + 2 \sum_{r=1}^n \mu_r a_r^2 b_r^2 \right], \end{aligned}$$

since $a_r^2 + b_r^2 + 2a_r b_r = 1$.

Hence

$$\theta^4 = \frac{6}{\frac{1}{15} + 2 \sum_{r=1}^n \mu_r a_r^2 b_r^2}$$

and

$$\omega^2 = \frac{3EI}{\rho A l^4 \sum_{r=0}^n \mu_r a_r^2 b_r^2}, \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \dots \dots \dots (14)$$

where $\mu_0 a_0^2 b_0^2 = \frac{1}{30}.$

The mass of the shaft is taken as equivalent to a concentrated mass $\frac{8}{15} \rho A l$ placed at the mid-point.

If ω_0 be the lowest whirling speed for such a mass when the other loads are removed, and if $\omega_1, \omega_2, \dots \omega_n$ be the whirling speeds due to each of the separate masses acting alone on a mass-less shaft, (14) is equivalent to

$$\frac{1}{\omega^2} = \frac{1}{\omega_0^2} + \frac{1}{\omega_1^2} + \dots + \frac{1}{\omega_n^2}, \quad \dots \dots (15)$$

which is Dunkerley's rule.

The occurrence of (15) depends only on the neglect of powers of θ^4 , and Dunkerley's rule would result whatever the end conditions and whether the shaft is uniform or of varying section.

It is, however, by no means obvious that the neglect of the higher terms is justified, for θ is, in most cases, not a small quantity. Thus, for a uniform shaft, $\theta = \pi$. The assumption made is, therefore, that the coefficients of higher powers of θ are extremely small, and this will only be the case if the whirling speeds form a sequence in which the terms increase rapidly. It is thus evident that Dunkerley's rule is quite without justification until the magnitude of the other coefficients in the series has been examined.

4. The Error in Dunkerley's Rule*.

For a uniform unloaded shaft the above method gives

$$\omega^2 = \frac{90 EI}{\rho A l^4},$$

as compared with the value

$$\omega^2 = \frac{\pi^4 EI}{\rho A l^4}$$

given by the ordinary method of analysis.

* Cf. Hahn, *loc. cit.*

The value of ω is therefore too low in the ratio

$$\sqrt{90} : \pi^2 = 0.96 : 1,$$

an error of 4 per cent.

In this simple case it is easy to extend the series to the θ^8 term. The equation then becomes

$$6 - \frac{1}{15} \theta^4 + .0000526 \theta^8 = 0.$$

This gives as a second approximation

$$\begin{aligned} \theta^4 &= 90 + .000789 \theta^8 \\ &= 90 + .000789 \times 90^2 \\ &= 96.39. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16) \end{aligned}$$

Using this figure to obtain a closer approximation, we have

$$\begin{aligned} \theta^4 &= 90 + .000789 \times (96.4)^2 \\ &= 97.3 \text{ approx.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17) \end{aligned}$$

This gives $\theta^4 = \pi^4$ exactly, to the number of figures taken.

Thus the inclusion of the third term is sufficient for accuracy, but if it is used only to give a second approximation, such as (16), the value of θ^4 is too low by about 1 per cent.

The magnitude of the third term in the series will now be investigated for the case when the shaft carries concentrated loads. To simplify the analysis, the mass of the shaft itself will be neglected.

If $\psi(x)$, $\chi(x)$ denote the integrals

$$\begin{aligned} &\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x f(x) dx \\ \text{and} \quad &\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x x^3 f(x) dx, \end{aligned}$$

the values of these functions, when only concentrated loads are taken into account, are

$$\begin{aligned} \psi(x) &= \left| \begin{array}{c} x < a_1. \\ 0 \end{array} \right| + \left| \begin{array}{c} x > a_1. \\ + \frac{1}{6} \mu_1 a_1 (x - a_1)^3 \end{array} \right| + \left| \begin{array}{c} x > a_2. \\ + \frac{1}{6} \mu_2 a_2 (x - a_2)^3 \end{array} \right| + \text{etc.} \\ \chi(x) &= \left| \begin{array}{c} 0 \end{array} \right| + \left| \begin{array}{c} + \frac{1}{6} \mu_1 a_1^3 (x - a_1)^3 \end{array} \right| + \left| \begin{array}{c} + \frac{1}{6} \mu_2 a_2^3 (x - a_2)^3 \end{array} \right| + \text{etc.} \end{aligned}$$

Also $f(x)=0$, except at $x=a_r$, $r=1, 2, \dots n$, and

$$\lim_{\epsilon \rightarrow 0} \int_{a_r-\epsilon}^{a_r+\epsilon} f(x) dx = \mu_r.$$

The following integrals are now required:—

| | $x < a_2$ | $x > a_2$ | $x > a_3$ | |
|---------------------------------------------------|-----------|----------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| $\int_0^x \psi(x)f(x) dx$ | 0 | $+\frac{1}{6}\mu_1\mu_2a_1(a_2-a_1)^3$ | $+\frac{1}{6}\mu_1\mu_3a_1(a_3-a_1)^3$ $+\frac{1}{6}\mu_2\mu_3a_2(a_3-a_2)^3$ | + etc. |
| $\int_0^x dx \int_0^x \psi(x)f(x) dx$ | 0 | $+\frac{1}{6}\mu_1\mu_2a_1(a_2-a_1)^3$ $(x-a_2)$ | $+\frac{1}{6}\mu_1\mu_3a_1(a_3-a_1)^3$ $(x-a_3)$ $+\frac{1}{6}\mu_2\mu_3a_2(a_3-a_2)^3$ $(x-a_3)$ | + etc. |
| $\int_0^x dx \int_0^x dx \int_0^x \psi(x)f(x) dx$ | 0 | $+\frac{1}{36}\mu_1\mu_2a_1(a_2-a_1)^3$ $(x-a_2)^3$ | $+\frac{1}{36}\mu_1\mu_3a_1(a_3-a_1)^3$ $(x-a_3)^3$ $+\frac{1}{36}\mu_2\mu_3a_2(a_3-a_2)^3$ $(x-a_3)^3$ | + etc. |

Hence

$$\begin{aligned} \int_0^1 dx \int_0^x \psi(x)f(x) dx &= \frac{1}{6} \sum_{r=1}^{n-1} \sum_{s=r+1}^n \mu_r \mu_s a_r (a_s - a_r)^3 (1 - a_s), \\ \int_0^1 dx \int_0^x dx \int_0^x \psi(x)f(x) dx &= \frac{1}{36} \sum_{r=1}^{n-1} \sum_{s=r+1}^n \mu_r \mu_s a_r (a_s - a_r)^3 (1 - a_s)^3. \end{aligned}$$

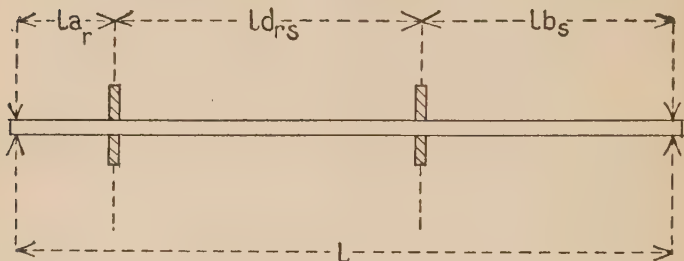
These may conveniently be written as follows:—

$$\left. \begin{aligned} \int_0^1 dx \int_0^x \psi(x)f(x) dx &= \frac{1}{6} \sum_{r,s=1}^n \mu_r \mu_s a_r b_s d_{rs}^3, \\ \int_0^1 dx \int_0^x dx \int_0^x \psi(x)f(x) dx &= \frac{1}{36} \sum_{r,s=1}^n \mu_r \mu_s a_r b_s^3 d_{rs}^3, \end{aligned} \right\} \quad (18)$$

where ld_{rs} is the distance between the two loads, and the

summation is for all pairs of loads in the relative positions shown in fig. 1.

Fig. 1.



In a similar way,

$$\left. \begin{aligned} \int_0^1 dx \int_0^x \chi(x) f(x) dx &= \frac{1}{6} \sum_{r,s=1}^n \mu_r \mu_s a_r^3 b_s^3 d_{rs}^3, \\ \int_0^1 dx \int_0^x dx \int_0^x \chi(x) f(x) dx &= \frac{1}{36} \sum_{r,s=1}^n \mu_r \mu_s a_r^3 b_s^3 d_{rs}^3. \end{aligned} \right\} \quad (19)$$

Hence, including the θ^3 terms,

$$\left. \begin{aligned} f_2(1) &= 1 + \frac{1}{6} \theta^4 \sum_{r=1}^n \mu_r a_r b_r^3 + \frac{1}{36} \theta^8 \sum_{r,s=1}^n \mu_r \mu_s a_r b_s^3 d_{rs}^3, \\ f_2''(1) &= \theta^4 \sum_{r=1}^n \mu_r a_r b_r + \frac{1}{6} \theta^8 \sum_{r,s=1}^n \mu_r \mu_s a_r b_s d_{rs}^3, \\ f_4(1) &= 1 + \frac{1}{6} \theta^4 \sum_{r=1}^n \mu_r a_r^3 b_r^3 + \frac{1}{36} \theta^8 \sum_{r,s=1}^n \mu_r \mu_s a_r^3 b_s^3 d_{rs}^3, \\ f_4''(1) &= 6 + \theta^4 \sum_{r=1}^n \mu_r a_r^3 b_r + \frac{1}{6} \theta^8 \sum_{r,s=1}^n \mu_r \mu_s a_r^3 b_s d_{rs}^3, \end{aligned} \right\} \quad (20)$$

and the equation for the whirling speed is

$$\begin{aligned} &6 - \theta^4 \sum_{r=1}^n \mu_r (a_r b_r - a_r^3 b_r - a_r b_r^3) \\ &+ \theta^8 \left[\frac{1}{6} \sum_{r=1}^n \mu_r a_r b_r^3 \sum_{r=1}^n \mu_r a_r^3 b_r - \frac{1}{6} \sum_{r=1}^n \mu_r a_r b_r \sum_{r=1}^n \mu_r a_r^3 b_r^3 \right. \\ &\left. - \frac{1}{6} \sum_{r,s=1}^n \mu_r \mu_s (a_r b_s - a_r b_s^3 - a_r^3 b_s) d_{rs}^3 \right] = 0, \quad (21) \end{aligned}$$

or

$$1 - \frac{1}{6}\theta^4 \sum_{r=1}^n 2\mu_r a_r^2 b_r^2 + \frac{1}{36}\theta^8 \sum_{r,s=1}^n \mu_r \mu_s a_r b_s \{a_s b_r (a_s^2 - a_r^2)(b_r^2 - b_s^2) - (1 - a_r^2 - b_s^2) a_{rs}^3\} = 0, \quad (22)$$

where, in the last term, the summation includes each pair of masses once only.

If (22) is written

$$1 - \frac{1}{6}p\theta^4 + \frac{1}{36}q\theta^8 = 0, \quad . \quad . \quad . \quad (23)$$

the second approximation to the least value of θ is given by

$$\begin{aligned} \theta^4 &= \frac{6}{p} + \frac{q}{6p}\theta^8 \\ &= \frac{6}{p} \left(1 + \frac{q}{p^2}\right). \quad . \quad . \quad . \quad (24) \end{aligned}$$

The magnitude of the correction given by the term $\frac{q}{p^2}$ is shown in the following table for the case when the masses are equal and equally spaced:—

| No. of Masses. | Value of $\frac{q}{p^2}$. | Percentage change in value of ω made by including this term. |
|----------------|----------------------------|---------------------------------------------------------------------|
| 2 | ·0586 | nearly 3 per cent. |
| 3 | ·0675 | „ 3·5 „ „ |
| 4 | ·0698 | „ 3·5 „ „ |
| 5 | ·0707 | about 3·5 „ „ |
| 6 | ·0709 | „ 3·5 „ „ |
| 7 | ·071 | „ 3·5 „ „ |
| 9 | ·071 | „ 3·5 „ „ |
| ∞ | ·071 | „ 3·5 „ „ |

The last value has been obtained by expressing the limiting value of $\frac{q}{p^2}$, as given by (22), in the form of a double integral.

The result, as might be expected, is identical with that given by the analysis leading to equation (16).

The remarkable thing about these figures is the rapidity with which the limiting value is approached as n increases,

so that the correction is systematically in the neighbourhood of 3·5 per cent.

As in the case of the uniform shaft, this correction is raised to 4 per cent. by carrying the approximation a stage further. We have, in fact, from the equation

$$\theta^4 = \frac{6}{p} + \frac{q}{6p} \theta^3$$

the approximate value

$$\begin{aligned} \theta^4 &= \frac{6}{p} \left(1 + \frac{q}{p^2} + \frac{2q^2}{p^4} + \frac{q^3}{p^6} \right) \\ &= \frac{6}{p} (1\cdot0814), \end{aligned}$$

when q/p^2 has the value ·071. This gives the correction of 4 per cent. which, accurate in the case of a uniform mass, will be very nearly so for concentrated masses*.

A revised form of the rule can now be given from the consideration that, if a multiplier is introduced which corrects the term due to the mass of the shaft itself, the whole expression will be simultaneously corrected, to a fair degree of approximation. Thus for a shaft carrying concentrated masses, the mass of the shaft itself not being negligible, the first whirling speed is given by

$$\frac{\alpha}{\omega^2} = \frac{1}{\omega_0^2} + \sum_{r=1}^{r=n} \frac{1}{\omega_r^2}, \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where α , ω_0^2 , ω_r^2 are given for various types of support in the table below. All the values are obtainable by analysis similar to the above.

| Type of Bearings. | α^2 . | ω_0^2 . | ω_r^2 . |
|-------------------------------|--------------|-------------------|------------------------------------------|
| Both short | 1·08 | $90EI/\rho Al^4$ | $3EI/m_r a r^2 h_r^2$ |
| Both long | 1·168 | $420EI/\rho Al^4$ | $3EI l^3/m_r a r^3 b_r^3$ |
| One short, one long† | 1·12 | $210EI/\rho Al^4$ | $12EI l^3/m_r a r^3 b_r^2 (3a_r + 4b_r)$ |
| One long, shaft overhangs ... | 1·017 | $12EI/\rho Al^4$ | $3EI/m_r a r^3$ |

† $a_r l$ is here the distance from the long bearing.

When the attached masses divide the shaft into unequal segments, the error in Dunkerley's rule will be found in

* This limiting value of the correction is given by Hahn in the paper cited above. He does not, however, examine the convergence towards the limit.

general to be rather less than for the same number of equally placed masses. The variation in the error when only two masses are carried and one is moved along the shaft, the other remaining fixed, has been studied by Hahn*, who has also considered the effect of the finite size of the masses.

5. Non-Uniform Shaft.

If I_0 be the moment of inertia of the section at $x=0$, and if $\frac{I}{I_0} = \phi(x)$, the equation for y becomes

$$\frac{d^2}{dx^2} \left(\phi(x) \frac{d^2 y}{dx^2} \right) - \theta^4 f(x) y = 0, \quad \dots \quad (26)$$

where

$$\theta^4 = \frac{\rho A \omega^2 l^4}{EI_0} \dots \dots \dots (27)$$

The solution of equation (26) is easily seen to be

$$y = Af_1(x) + Bf_2(x) + Cf_3(x) + Df_4(x),$$

where

$$\left. \begin{aligned} f_1(x) &= 1 + \theta^4 \int_0^x dx \int_0^x \frac{dx}{\phi(x)} \int_0^x dx \int_0^x f(x) dx + \dots, \\ f_2(x) &= x + \theta^4 \int_0^x dx \int_0^x \frac{dx}{\phi(x)} \int_0^x dx \int_0^x x f(x) dx + \dots, \\ f_3(x) &= \int_0^x dx \int_0^x \frac{dx}{\phi(x)} \\ &\quad + \theta^4 \int_0^x dx \int_0^x \frac{dx}{\phi(x)} \int_0^x dx \int_0^x f(x) dx \int_0^x dx \int_0^x \frac{dx}{\phi(x)} + \text{etc.} \\ f_4(x) &= \int_0^x dx \int_0^x \frac{x dx}{\phi(x)} \\ &\quad + \theta^4 \int_0^x dx \int_0^x \frac{dx}{\phi(x)} \int_0^x dx \int_0^x f(x) dx \int_0^x dx \int_0^x \frac{x dx}{\phi(x)}. \end{aligned} \right\} \dots \dots (28)$$

In these, let $\phi(x)$ be any function, while $f(x)$ is zero except at special points.

To obtain the first approximation it is sufficient to consider a shaft carrying only one load. If the ends are in

* *Loc. cit.*

short bearings, the end conditions will lead to equation (10), as before. The values of the functions involved are, neglecting θ^3 ,

$$\left. \begin{aligned} f_2(1) &= 1 + \mu a \theta^4 \int_a^1 dx \int_a^x \frac{(x-a)}{\phi(x)} dx, \\ f_2''(1) &= \frac{\mu a \theta^4 (1-a)}{\phi(1)}, \\ f_4(1) &= \int_0^1 dx \int_0^x \frac{dx}{\phi(x)} + \mu \theta^4 \int_a^1 dx \int_a^x \frac{x-a}{\phi(x)} dx \times \int_0^a dx \int_0^x \frac{x dx}{\phi(x)}, \\ f_4''(1) &= \frac{1}{\phi(1)} \left[1 + \mu(1-a) \int_0^a dx \int_0^x \frac{x dx}{\phi(x)} \right]. \end{aligned} \right\} \quad \dots (29)$$

When these are substituted in (10), the equation for θ^4 is

$$\mu \theta^4 \left[ab \int_0^1 dx \int_0^x \frac{dx}{\phi(x)} - a \int_a^1 dx \int_a^x \frac{x-a}{\phi(x)} dx - b \int_0^a dx \int_0^x \frac{x dx}{\phi(x)} \right] = 1. \quad \dots (30)$$

It is not difficult to verify that the quantity in the bracket is equal to

$$\frac{EI_0}{l^4} \delta,$$

where δ is the deflexion that would be caused at the position of the load by a transverse unit force acting there on the shaft. Hence

$$\omega^2 = \frac{1}{M\delta}, \quad \dots (31)$$

as is otherwise evident.

If the series is carried to the term in θ^3 , a correction term is obtained equivalent to that given by Prof. Jeffcott's analysis. The advantage of the present method is that it enables concentrated loads and distributed loads to be treated together.

From the analogy of the uniform shaft, it is likely that the θ^3 term will give almost the whole of the correction needed for the first whirling speed, and that the corrections needed when the shaft carries concentrated loads will not be very different from those required for distributed loads.

The following method is therefore suited to give the first

whirling speed of a non-uniform shaft carrying concentrated masses in addition to a distributed load :—

(1) By means of equations (28), let first and second approximations to the whirling speeds be found when the concentrated masses are removed. Let the first approximation be ω_0 , and the second, which will be nearly exact, $a\omega_0$.

(2) From (30) find ω_r^2 for each concentrated load.

(3) The whirling speed is then given by

$$\frac{a^2}{\omega^2} = \frac{1}{\omega_0^2} + \sum_{r=1}^n \frac{1}{\omega_r^2} \cdot \cdot \cdot \cdot \quad (25 \text{ bis})$$

CXIV. *The Magnetic Properties of Atoms and Molecules.*

By BERNARD HOWELL WILSDON*.

IN two previous papers (*suprà*, pp. 354, 900) a theory of the polar and non-polar chemical link has been developed on the basis of quantum exchanges between valency orbits involving half numbers. The non-polar link was treated in a manner similar to that which was successfully employed by Sommerfeld in explaining the anomalous Zeeman effect. The polar link was attacked from the standpoint of the Stark effect. In both treatments the fundamental postulate was adopted that precessional or nutational movements of the orbits which form the chemical bond synchronize the frequencies of the naturally untuned orbits, in a manner whereby the total moment of momentum in opposite directions of the bond is equalized. By this means, with simple and consistent assumption as to quantum changes, the heats of formation of various simple bodies were calculated and reasonably good agreement with experimental values was obtained. The application of the fundamental postulate of the synchronization of frequencies, together with the principle of spatial quantizing, should enable us to draw definite and quantitative conclusions as to the magnetic and stereometric properties of the molecule. In calculating the energy changes consequent on combinations of atoms, we assumed that the component of the moment of momentum in a direction at right angles to "the equatorial plane" of the molecule must be equal and opposite for each atom. The residual moments of the valency electron or electrons must then all lie along axes which lie in the equatorial plane. The two halves of the

* Communicated by the Author.

molecule must behave as rigid systems, since by spatial quantizing the inclination as well as the size of the orbits is fixed. The orientation of the axes which lie in the equatorial plane is, of course, not subject to spatial quantizing; they are free to rotate about the molecular axis, so long as their inclination thereto does not change. Since no energy change is involved in such displacements, the orientation of such axes will be determined by probability considerations.

Synchronization of the orbital movements of the electrons belonging to different parts of the molecule will be brought about by precessional rotations in opposite senses of the systems. It is these rotations which bring the moments of the two systems into equilibrium. No assumption need be made as to a necessary equality in the number of valency orbits associated with each atom in combination, nor is it necessary to suppose that the electrons of the different atoms move in joint orbits. So long as the axial components of the moments are equal and opposite on both sides of the equatorial plane, and the rotations of the electrons in their orbits synchronize, the conditions for chemical combination are fulfilled. As an example of the arrangement of orbits postulated, we may take the case of nitric oxide. Four electrons of each atom belonging to the k_1 group may lock up together into a configuration of zero moment similar to the valency shell surrounding a rare gas. This leaves two k_2 orbits belonging to the oxygen, and one for the nitrogen. Alternatively we may suppose that five electrons from the oxygen and one from the nitrogen lock up, leaving one free oxygen valency and three free nitrogens. The underlying group of six electrons in this case corresponds to one of the stable sub-groups shown by Bohr's well-known arrangement. Equilibrium across the equatorial plane would then be obtained by orientating $3(k=3/2)$ nitrogen electrons at $\cos \theta = 1/3$ and $1(k=3/2)$ oxygen electron at $\cos \theta = 1$. It may be expected that such an arrangement will give rise to a free moment, as is found to be the case. It will be shown that models of this character will give quantitative explanations of the magnetic properties of atoms and molecules on the basis of the simple assumptions outlined above.

For simplicity we regard the electrons as occupying their time mean positions in their Kepler orbits. These orbits will precess in the molecular magnetic field, so the problem will reduce itself to calculating the moment of the system in its rotations about the precessional axis. Since the system is rigid, if we take a point of reference which is fixed in space and which we may regard as situated in one or other

of the atomic nuclei, it is easy to deduce from d'Alembert's principle that

$$\frac{dq'}{dt} = Vpq - L. \quad (1)$$

Here the p 's are the moments of momenta and the q 's are angular velocities; L is the mechanical moment. q' is a velocity referred to an origin which rotates with the rigid system. dq'/dt must be equal to zero; so we may write

$$Vpq = L. \quad (2)$$

Since the p 's and q 's must necessarily be related, we may introduce an operator which transforms the vector q into p . This operator may be written as the sum of a symmetrical linear operator and the vector product of another vector f , so that

$$p = \Omega q + Vf q. \quad (3)$$

Equation (2) may thus be written:

$$L = q\Omega q + Vq Vf q. \quad (4)$$

Since L is a vector magnitude, it must be related to the resultant magnetic moment of the molecule and the field as follows:

$$L = V\mu H. \quad (5)$$

If we consider an isolated molecule for which we have fixed in space a point of reference in one of its nuclei, its paramagnetism must be a vector quantity determined by the intrinsic properties of the molecular structure. A diamagnetic molecule, on the other hand, only develops a magnetic moment when we also determine the direction and magnitude of an external field. This is seen at once from equation (4), for since Ω is symmetrical, the first term is zero, so that the free moment is zero in the absence of an external field. The "susceptibility" of a molecule measures the rate of change of the magnetic moment with the strength of an imposed magnetic field. For a fixed paramagnetic molecule the susceptibility should therefore be zero, since its free moment is not dependent on the strength of the field (this assumes, of course, that we are dealing with a simple molecule composed of only two atoms). The susceptibility, so called, of a paramagnetic substance as measured in the gaseous or liquid state will thus be a probability function of the temperature which may be written $\frac{\mu}{H} \frac{\partial x}{\partial y}$ where x and y are unit vectors determining the directions of the magnetic

moment and field respectively. For a diamagnetic molecule, on the other hand, we measure the quantity $\frac{x}{y} \frac{\partial \mu}{\partial H}$, where

$\frac{\partial \mu}{\partial H}$ will be an intrinsic property of the molecule and $\frac{x}{y}$ fixed

by probability considerations. Since no particular direction in a simple diamagnetic molecule will be favoured in a random assemblage, this function will be a constant independent of the temperature, so long as the electronic structure does not undergo a change, as is well known to be the case in most simple substances.

In order to obtain an expression for the diamagnetism of the molecule, we may proceed as follows:—

Multiplying (4) by the Hamiltonian operator, we have

$$\nabla V \mu H = \nabla V q V f q + \nabla V q \Omega q,$$

so that

$$H \text{ curl } \mu = V f q \text{ curl } q + \Omega q \text{ curl } q - q \text{ curl } \Omega q.$$

$\Omega q \text{ curl } q$ is equal to zero; if we limit consideration first to a symmetrical molecule, we may ignore $V f q$ and write

$$H \text{ curl } \mu = -q \text{ curl } \Omega q. \quad . \quad . \quad . \quad (6)$$

Now a precessional rotation \mathbf{O} is related to a vector magnetic field by the well-known Lorentz expression

$$\mathbf{O} = \frac{eH}{2mc}. \quad . \quad . \quad . \quad (7)$$

The angular velocity of our rotating rigid system q may thus be equated to \mathbf{O} .

Substituting (7) in (6), we then have

$$H \text{ curl } \mu = -\frac{eH}{2mc} \text{ curl } \Omega q$$

or

$$\mu = -\frac{e}{2mc} \Omega q.$$

Writing q as the product of a scalar q into the unit vector \mathbf{x} and again substituting (7), we have

$$\mu = -\frac{e^2}{4m^2c^2} H \Omega \mathbf{x} = -\frac{e^2}{4m^2c^2} H y \Omega \mathbf{x},$$

where y is a unit vector defining H , so that

$$\frac{\partial \mu}{\partial H} = -\frac{e^2}{4m^2c^2} y \Omega \mathbf{x}. \quad . \quad . \quad . \quad (8)$$

In order to calculate the paramagnetism, (4) may be written, since $\mathbf{Vq}\Omega\mathbf{q}$ is zero,

$$\mu\mathbf{H}\mathbf{V}\mathbf{xy}=(q^2)\mathbf{f}-(\mathbf{qf})\mathbf{q}.$$

The direction of the atomic or molecular field \mathbf{H} must be the same as that of the resultant angular velocity \mathbf{q} , so that

$$\mu\mathbf{H}=q^2\mathbf{f}\mathbf{V}\mathbf{xy}-(\mathbf{qf})\mathbf{q}\mathbf{V}\mathbf{xy}. \quad . \quad . \quad . \quad (9)$$

The last term of this equation is zero, since the vector product $\mathbf{V}\mathbf{xy}$ is at right angles to the direction of \mathbf{q} . This follows from the consideration that the internal field of the paramagnetic molecule must be in the same direction as the vector which determines the axis of the angular velocity \mathbf{q} . Dividing by \mathbf{H}^2 from (7), we then have

$$\frac{\mu}{\mathbf{H}}=\frac{e^2}{4m^2c^2}\mathbf{f}\mathbf{V}\mathbf{xy}=\frac{e^2}{4m^2c^2}\mathbf{y}\mathbf{V}\mathbf{fx}. \quad . \quad . \quad . \quad (10)$$

Multiplying by \mathbf{y} , we see at once that the free moment μ is at right angles to the direction of \mathbf{x} .

We have now to develop the operators Ω and \mathbf{Vf} . Their form may be seen from the following simple considerations.

The moment of momentum p is equal to $\Sigma\frac{d\mathbf{E}_{\text{kin}}}{dq}$. Considering for simplicity that the electrons of the precessing orbits are fixed in their time mean positions, we may write for the kinetic energy due to their precessional movements

$$\mathbf{E}_{\text{kin}}=\Sigma\frac{m}{2}(\dot{r}^2+r^2q^2).$$

The time mean value of \dot{r} is zero, so

$$p=\Sigma\frac{m}{2}r^2\frac{dq^2}{dq}=\Sigma mr^2q.$$

The operators are thus of the form Σmr^2 . This means that we have to deal with an "inertial" operator as in the ordinary case of Poincot motion. The time mean displacements can now be calculated in terms of the azimuthal and principal quantum numbers of the orbits. It has been shown (*c.f.* Sommerfeld, 'Atomic Structure,' Eng. trans. p. 313) that $r=3/2a\epsilon$, where a is the major axis of the Kepler ellipse and ϵ is the eccentricity. The eccentricity is given by the factor

$$\epsilon=\sqrt{1-\frac{k^2}{n^2}},$$

where n and k represent the principal and azimuthal quantum

numbers respectively. r thus becomes equal to

$$r = \frac{3}{2} \frac{h^2}{4\pi^2 m e^2 Z} \cdot n \sqrt{n^2 - k^2}, \quad \dots \quad (11)$$

where Z is the effective atomic number.

In what follows we consider only the inertia components of the valency electrons. By neglecting the inertias of the nucleus and inner electrons we shall not make a great error. The energy of the nucleus can only represent a small heat term; a quantum group in the shell next below the valency rings, when complete, must be symmetrical, and thus will not contribute to the inertia terms. This is not the case when the shell next below the valency shell is incomplete, as it is in the transition elements; it will be shown later that the strong paramagnetism of these elements is to be attributed to this fact. Since then the mass term of our inertial operator is constant and equal to that of the electron, we need consider only the squares of the time mean displacements r^2 . Call these R_i ; for each orbit there will then correspond an axis which we assume is uniquely occupied for the reason that two orbits, orientated in the same direction and belonging to the same atom but having different parameters, would inevitably entail a collision when subjected to an external field. Moreover, we have no reasons for assuming that the same orbit can be occupied by two electrons. We may then choose for convenience as many axes, $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \dots \mathbf{x}_i$, as there are active valency electrons in the atom. If we distinguish one of them, \mathbf{x}_1 , as that normal to the equatorial plane of the molecule, it will be convenient to place the remainder on the equatorial plane. We may now write the two operators Ω and Vf in terms of conjugate components R and R' , where Ω is the arithmetical mean of R and R' . R and R' must be identified in our present case with the inertial components on either side of the same axis; but since we assume constantly that the sense of the rotation reverses on either side of the axis, we shall write

$$\Omega = \frac{1}{2}(R - R').$$

$\Omega \mathbf{x}$ then becomes simply

$$\frac{1}{2} \{ \mathbf{x}_1(R_1 - R'_1) + \mathbf{x}_2(R_2 - R'_2) + \mathbf{x}_3(R_3 - R'_3) \dots \}, \quad (12)$$

where $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \dots$ are the components of the vector \mathbf{x} distinguishing the various axes. $Vf \mathbf{x}$ is then the determinant:

$$\frac{1}{2} \begin{vmatrix} 1 & 1 & 1 \\ \mathbf{x}_1 & \mathbf{x}_2 & \mathbf{x}_3 \\ (R_1 + R'_1) & (R_2 + R'_2) & (R_3 + R'_3) \end{vmatrix} \dots \quad (13)$$

We may, however, immediately simplify these expressions by assuming for the present that the precessional rotation of which \mathbf{x} is the unit vector is normal to the equatorial plane. If, then, $\mathbf{x}_2, \mathbf{x}_3 \dots$ are regarded as situated in this plane, (12) reduces simply to $\frac{1}{2}\mathbf{x}(R_1 - R_1')$, and (13) to

$$\frac{1}{2}\{(R_2 + R_2') - (R_3 + R_3')\}\mathbf{x}. \quad \dots \quad (14)$$

It is to be noted that we are only justified in regarding R and R' as conjugated in the manner shown, on the basis of our fundamental assumption that $\mathbf{p} = \mathbf{p}'$; i.e., that the precessional rotations bring the moment of momentum into equilibrium. R and R' may be regarded as belonging to different atoms of the molecule, or they may refer to orbits of the same atom. In the one case the equatorial plane will be placed at right angles to the "bond"; in the other it must lie in the atomic nucleus. For an atom, the effective atomic charge and the principal quantum number must be constant in both terms; in the molecule, however, both the atomic charge and the principal quantum number may vary. Introducing these expressions into equations (8) and (9), we shall have

$$\frac{\partial \mu}{\partial H} = - \frac{e^2}{4m^2c^2} \cdot \frac{m}{2} \left(\frac{3h^2}{8\pi^2me^2} \right)^2 \left\{ \frac{R_1}{Z^2} - \frac{R_1'}{Z'^2} \right\} \mathbf{yx} \quad (15)$$

and

$$\frac{\mu}{H} = \frac{e^2}{4m^2c^2} \cdot \frac{m}{2} \left(\frac{3h^2}{8\pi^2me^2} \right)^2 \left\{ \frac{R_2 - R_3}{Z^2} + \frac{R_2' - R_3'}{Z'^2} \right\} \mathbf{yx}. \quad \dots \quad (16)$$

The constant term becomes, on substitution of the appropriate values of the constants and multiplying by Avogadro's number,

$$D = \frac{9 \times (6.55 \cdot 10^{-27})^4 \times (606 \cdot 10^{24})}{512 \times (3.142)^4 \times (.899 \cdot 10^{-27})^3 \times (1.591 \cdot 10^{-20})^2 \times (3.10^{10})^2} = 1.350 \cdot 10^{-6}.$$

Introducing the values of R defined by the quantum factor of (11), we have finally for the expression of the diamagnetism χ_d ,

$$\chi_d = -D \left\{ \frac{n_1'^2(n_1'^2 - k_1'^2)}{Z^2} - \frac{n_1'^2(n_1'^2 - k_1'^2)}{Z'^2} \right\} \mathbf{yx}, \quad (17)$$

while the paramagnetism χ_p becomes

$$\chi_p = D \left\{ \frac{n_2^2(n_2^2 - k_2^2) - n_3^2(n_3^2 - k_3^2)}{Z^2} + \frac{n_2'^2(n_2'^2 - k_2'^2) - n_3'^2(n_3'^2 - k_3'^2)}{Z'^2} \right\} \mathbf{yx}. \quad (18)$$

The factor \mathbf{yx} represents the cosine of the angle made by the directions of the field and the magnetic moment. This we calculate from simple probability considerations. If there is only one direction in the molecule in which there is a magnetic moment (paramagnetic body) or in which a moment can be induced (diamagnetic), the average inclination will be given by $\cos^2 \theta = \frac{1}{3}$, as in the well-known Langevin formula; if there are two such directions this factor will become $\frac{1}{2}$, while for three or more axes, which, of course, can all be resolved about three principal axes, simply 1. We thus put in the three cases $\cos \theta = 1/\sqrt{3}$, $1/\sqrt{2}$, and 1 respectively. In the case of a paramagnetic substance, Sommerfeld ('Atomic Structure,' Eng. trans. p. 250) has suggested quantizing these angles in terms of the possible values which can be adopted by the azimuthal quantum number of the orbits. On the present theory all values which can be adopted by the equatorial and latitudinal quantum numbers are not admissible, so the method must be rejected.

In order to test these equations, we may first consider diamagnetic molecules which can be regarded as dipoles. It will then be necessary to make some consistent assumption as to the effective atomic numbers. If we regard the molecule as linked by a single bond in the chemical sense, or if we have to deal with an atom which has a single electron in the valency shell, we assume that the effective atomic number is unity. In the case of the metals in the first group of the periodic table, this assumption will be readily conceded; with such effectively monovalent elements as the halogens, our assumption depends on the electronic constitution we assign to the shell below the valency shell. As we shall have to refer repeatedly to this shell, it will be a convenience to number our shells from the outside inwards, instead of by the commonly adopted spectroscopic convention of numbering them from the nucleus outwards. If we call the valency shell V, let us call the one below W. It will probably not be necessary to go deeper into the constitution of the atom. In a halogen molecule, as already explained, we assume a joint W shell. For chlorine and elements of higher atomic number this shell is composed of two groups of six electrons each. Fluorine is not able to assume this configuration, as its X shell, which is the same as that usually designated K, would then only contain two electrons; the shell of eight electrons, which must intervene between a K ring and an M shell containing groups of six, would be absent. Fluorine will be anomalous in this respect therefore, in that it cannot be regarded as effectively monovalent like

the other halogens. This fixing of the effective atomic number is, of course, purely arbitrary, and can only be justified by results. The mechanism by which this change comes about, and which may eventually afford a quantitative account of the process, appears reasonably clear. On combination of two atoms, our fundamental postulate states that the energy represented by the difference of the two terms representing the natural frequency of the valency electrons of the uncombined atoms becomes "available." Part of this energy goes to alter the kinetic energy of the electrons so that their frequencies are synchronized; part is absorbed in the molecular structure as potential energy, and the excess or deficit becomes "free" and represents the heat of the reaction. Although not at present mathematically demonstrable, we assume that this potential energy is responsible for changing the effective atomic numbers of the molecule. The ratios of the kinetic and potential energies in the magnetic field we have calculated (*loc. cit.*). In the magnetic field it was shown that

$$E_{\text{kin}} = -\frac{3}{2} E_{\text{pot}} \dots \dots \dots (19)$$

This relation has made possible the calculation of heats of reaction of simple substances by using as effective atomic numbers for the uncombined atoms those which result by subtracting the Sommerfeld screening number corresponding to the number of free valency electrons from the number which locates the element in the appropriate vertical column of the periodic table. For the purposes of calculating the magnetic properties, we here assume the molecular effective atomic number; an atom will still retain the effective atomic number calculated as before. A difficulty arises in the case of a rare gas, or an atom, significantly for example iron, which has a complete quantum group for its V shell. According to its position in the periodic table the effective atomic number of such atoms should be zero, which would make the para- or diamagnetism infinite. The actual number must therefore be small. It will be seen in what follows that the very high dia-magnetism of the rare gases, and the exceptional para-magnetism of iron, can be explained on this hypothesis, and an empirical number found which will account quantitatively for the observed results.

The precessional rotations which respond to the imposed magnetic field in diamagnetic atoms are those which depend on the asymmetry of the k numbers of the orbits. In a polar molecule, as has been emphasized in the well-known octet theory of Lewis and Langmuir, each ion attains a rare

gas V shell by exchange of electrons; this same hypothesis was used in calculating the heats of formation of polar molecules. The diamagnetism of such compounds should then be calculated as the sum of the individual values of the ions which are regarded as atoms with eight valency electrons, but with atomic numbers of $+1$ and -1 respectively. As the effective atomic number enters as the square, Z^2 is 1 in both cases. Equation (17) then shows that diamagnetism will be given by

$$\chi_d = -D \{ [n_1^2(n_1^2 - k_1^2) - n_1^2(n_1^2 - k_1'^2)] + [n_2^2(n_2^2 - k_2^2) - n_2^2(n_2^2 - k_2'^2)] \} \cos \theta. \quad (20)$$

Here the numerical suffixes 1 and 2 refer to the different ions and not to the axis concerned. For each ion the principal quantum numbers n_1 and n_2 are constant. The paramagnetism according to equation (16) must obviously be zero. The expression then simply reduces to

$$\chi_d = -D \{ n_1^2(k_1'^2 - k_1^2) + n_2^2(k_2'^2 - k_2^2) \} \cos \theta.$$

The pairs of electrons belonging to each atom must have different values of k and k' . By the hypothesis of exchanges of half quantum numbers with the nucleus or trunk, in the manner Sommerfeld and Pauli have employed in calculating the anomalous Zeeman effect, an azimuthal quantum number of 2 becomes $3/2$ and one of 1 becomes $1/2$. This hypothesis is employed consistently in all that follows.

Since $(k_1'^2 - k_1^2) = (k_2'^2 - k_2^2) = (9/4 - 1/4)$, and $\cos \theta$ must be $\sqrt{1/3}$, we shall have simply

$$\chi_d = -\frac{2D}{\sqrt{3}} (n_1^2 + n_2^2). \quad . \quad . \quad . \quad (21)$$

Table I. gives the results obtained by calculating on the above formula the values of the diamagnetism for the compounds shown. The experimental results are taken from Landolt and Börnstein (1924 edition). The values χ_M used are the arithmetical means of the observed values multiplied by the molecular weight. In the divalent compounds, simply twice the value for the halogen ion has to be taken in the theoretical formula. It will be seen that in the case of the alkali metals and alkaline earths the agreement is as good as can be expected when the inaccuracy of the experimental results is considered. The fluorides are, however, distinctly abnormal, as was to be expected and as has been consistently observed in previous work. The experimental results are not sufficiently reliable to warrant

TABLE I.
Polar Compounds.

| | $\chi_m \times 10^6$. | $\chi_M \times 10^6$. | n_1 . | n_2 . | $\frac{(n_1^2 + n_2^2) \times 2.70}{\sqrt{3}}$. |
|-------------------------|------------------------|------------------------|---------|---------|--------------------------------------------------|
| NaCl | -0.41, -0.58 | -29.0 | 3 | 3 | -28.0 |
| NaBr | -0.37 | -38.1 | 3 | 4 | -38.9 |
| NaI | -0.31, -0.45 | -57.0 | 3 | 5 | -53.0 |
| KCl | -0.47, -0.55 | -36.5 | 4 | 3 | -39.0 |
| | -0.45 | | | | |
| KBr | -0.35, -0.45 | -47.6 | 4 | 4 | -49.9 |
| KI | -0.31, -0.45 | -63.1 | 4 | 5 | -63.9 |
| LiCl | -0.46 | -19.5 | 1 | 3 | -20.26 |
| MgCl ₂ | -50, -0.46, -45 | -44.6 | 3 | 3 | -42.1 |
| CaCl ₂ | -43, -41, -43 | -46.6 | 4 | 3 | -53.0 |
| SrCl ₂ | -44, -40 | -66.2 | 5 | 3 | -67.0 |
| SrBr ₂ | -31 | -76.8 | 5 | 4 | -88.8 |
| SrI ₂ | -35 | -119.4 | 5 | 5 | -117.0 |
| BaCl ₂ | -32, -41, -32 | -72.6 | 6 | 3 | -84.2 |
| BaBr ₂ | -31, -41 | -107.1 | 6 | 4 | -106.0 |
| BaI ₂ | -41, -30 | -140.8 | 6 | 5 | -134.0 |
| NaF | -40 | -16.82 | 3 | 2 | -20.2 |
| KF | -45 | -23.2 | 4 | 2 | -31.2 |
| CaF ₂ | -30 | -17.4 | 4 | 2 | -37.4 |
| SrF ₂ | -26 | -27.4 | 5 | 2 | -81.4 |
| BaF ₂ | -13 | -20.2 | 6 | 2 | -68.6 |
| ZnCl ₂ | -15 | -68.2 | 4 | 3 | -53.0 |
| HgCl ₂ | -24 | -66.4 | 6 | 3 | -84.2 |
| HgBr ₂ | -26 | -93.8 | 6 | 4 | -106.0 |
| AgCl | -28 | -40.1 | 5 | 3 | -53.0 |
| AgBr | -26 | -48.9 | 5 | 4 | -63.9 |
| AgI | -29 | -68.1 | 5 | 5 | -77.9 |

attempting to discover the appropriate relation. We may require to adopt a different effective atomic number for the fluorine ion, or the ion may become paramagnetic. The results for the base and noble metals are similarly not so good as the other results. Silver appears uniformly high, as also do zinc and mercury. Here, again, the effective atomic number for atoms whose V shell is composed of three groups of six electrons may be greater than that for the usual eight.

The same method of calculating should enable us to arrive at the diamagnetism of the halogen elements. Here we assume, as we have done consistently in calculating the energy relations, that one of the atoms contains an activated orbit. The effective atomic number is constant in both

terms. The molecular diamagnetism should then be calculated precisely as above except that n_2 is equal to $n_1 + 1$. Since only one valency orbit is activated, the remaining orbits in both atoms will be symmetrical, and there will therefore be no paramagnetism. The values so obtained are shown below.

TABLE II.

| | $-\chi_m \times 10^6$. | n_1 . | n_2 . | $-\chi_d$ calc. $\frac{2Dn^2 + (n+1)^2}{\sqrt{3}}$ | $-\chi_M$ found. |
|---------|--------------------------------------|---------|---------|-------------------------------------------------------|------------------|
| Cl..... | 0.59 | 3 | 4 | 39.9 | 42.2 |
| Br ... | 0.21, 0.38, 0.40 0.403 | 4 | 5 | 68.9 | 60.0 |
| I | 0.39, 0.36, 0.35 0.40, 0.30, 0.37 | 5 | 6 | 95.1 | 99.0 |

Hydrogen should be calculable on our hypothesis that one atom becomes activated. We assume that the molecular azimuthal quantum number for this atom is $3/2$. This will be readily accepted, as obviously the moment of momentum of the activated atom must decrease. The susceptibility will then be given by

$$\chi_M = -D \frac{4(4-9/4) - 1(1-1/4)}{\sqrt{3}} = -4.87 \times 10^{-6}.$$

The value found by Také Soné for $-\chi$ is 1.982 for the atom or 3.995 for the molecule. Kammerling Onnes, however, arrives at the value 2.7 for the atom or 5.4 for the molecule. This latter value is quoted by Pascal (*Comptes Rendus*, clvi. p. 324, 1913) in support of a value of 2.93, which represents the average value for the increase in the diamagnetism in saturated hydrocarbons. The mean of Také Soné's and Onnes' values is nearly 4.7. A discrepancy of this magnitude would not be surprising, considering the difficulty of the experimental measurements. As regards the value for the diamagnetism of hydrogen in combination, it is extremely doubtful that this should have the same value as in molecular hydrogen. The following considerations afford a probable explanation of the reason for the approximate agreement noted by Pascal. For the diamagnetism of a

C—H bond on the present theory we should write

$$D \frac{4(4-9/4)-1(1-1/4)}{\sqrt{3}} = 4.87 \times 10^{-6};$$

i.e., the same value as for molecular hydrogen. For the C—C link we should have similarly

$$D \frac{4(4-9/4)-4(4-1/4)}{\sqrt{3}} = 6.236 \times 10^{-6}.$$

This is near the mean value given by Pascal (6.0).

On increasing the length of a chain in a saturated hydrocarbon, each additional carbon carries with it two hydrogens. The bonds by which they are attached cannot both possibly orientate themselves in the same direction as the external field. They will make an angle of $109^{\circ} 28'$ with one another. This angle, as has been pointed out in the previous paper, is a consequence of spatial quantizing; it represents the solid angles between four vectors, three of which make an angle whose cosine is $1/3$ with the direction of the field, and which are arranged symmetrically about the axis, the fourth being parallel with the field in the negative direction. The average angle which each bond will make with the field is thus $50^{\circ} 44'$. 4.87 multiplied by the cosine of this angle is 2.82 , which is reasonably near Pascal's average. The value for carbon will be correct, as each additional carbon only involves one extra C—C link. It is thus obvious that the additive constants extracted by Pascal do not represent the intrinsic susceptibilities of the atoms. These have to be multiplied by a probability factor; in fact, his constants do not give values for the *atom*, but rather for the bonds which that atom can form with other elements, a consideration which makes it obvious that spatial probabilities must be considered. The very valuable data which Pascal has compiled are, however, likely to be of great value in extending, along the lines developed here, our knowledge of molecular structure. The examination of this aspect of the subject is reserved for another communication. At present it will be advisable to take a general survey of the applicability of the theory.

Nitrogen calculated by the simple addition formula should have a susceptibility of

$$\frac{(4+9)D}{\sqrt{3}} = 10.13 \times 10^{-6}.$$

The value given by Také Soné is 7.42 . There is no doubt,

however, that we should be incorrect in calculating nitrogen as a simple monovalent compound. Since there are now three free valencies to each atom according to the scheme

$2 \begin{pmatrix} \cdot & \cdot \\ 2 & 2 \end{pmatrix} 2$, we are not justified in neglecting the operators

Ω_2 and Ω_3 of equation (12). Our formula should then be

$$\chi_a = -\frac{D}{Z^2} \{ \Omega_1 \mathbf{x}_1 + \Omega_2 \mathbf{x}_2 + \Omega_3 \mathbf{x}_3 \} \mathbf{y} \dots \quad (22)$$

The two electrons of like azimuthal quantum numbers of each atom will arrange themselves symmetrically in the equatorial plane; it is thus clear since $R_2 = R_3$, $R_2' = R_3'$ that the molecule cannot be paramagnetic. Of the R_1 and R_1' bonds, one must be derived from an excited orbit. Equation (22) thus becomes

$$\chi_m = -\frac{D}{Z^2} \left\{ \left[9 \left(9 - \frac{9}{4} \right) - 4 \left(4 - \frac{1}{4} \right) \right] \mathbf{x}_1 + 8\mathbf{x}_2 + 8\mathbf{x}_3 \right\} \mathbf{y} \quad (23)$$

We now have to consider the probabilities for the cosines $\mathbf{x}_1\mathbf{y}$, $\mathbf{x}_2\mathbf{y}$, and $\mathbf{x}_3\mathbf{y}$. If \mathbf{x}_1 , \mathbf{x}_2 , and \mathbf{x}_3 are at right angles, our probable angle will be $\cos 1$. For an atom with three valency electrons the effective atomic number will be $3 - 0.577 = 2.423$, where 0.577 is the Sommerfeld screening number for three electrons. Z^2 should thus be 5.867. The above factors should then give 14.2×10^{-6} . Také Soné's value expressed for the molecule is 14.82×10^{-6} .

Experimental results for solid compounds are well known to be liable to very considerable errors. It will be interesting to compare a few results for elements where experimental values can be relied on with a fair amount of accuracy. An *element* (atom) with an odd number of valency orbits should always be paramagnetic unless a diatomic molecule is formed. While the alkalis and alkaline earths are uniformly paramagnetic, the metals in the sub-groups of the first two columns of the periodic table are diamagnetic. This must mean either that they form diatomic molecules, or that the V electrons can lock up with one of the groups of six in the W shell to form a system of zero moment. Only elements which can exist in more than one stage of "oxidation" in the chemical sense would be expected to show this property. There are thus alternative methods of calculating the diamagnetism of these elements:—

(1) As monatomic "rare gas" atoms with the appropriate atomic number and $\cos \theta = 1$. χ_m will then be given by

$$\chi_d = -\frac{D}{Z^2} \left\{ n^2 \left(n^2 - \frac{1}{4} \right) - n^2 \left(n^2 - \frac{9}{4} \right) \right\} = -2 \frac{Dn^2}{Z^2} \quad (24)$$

The principal quantum number does not change. The value of χ_d so obtained will be that of an atom.

(2) As non-polar combinations similar to hydrogen. Here the principal quantum numbers differ by unity due to excitation of one orbit; $\cos \theta$ will be determined by the number of axes about which precession can occur as explained before. If there are three such axes as in the case of nitrogen, $\cos \theta$ will be 1.

Table III. gives the results for various elements calculated according to these methods. The experimental values of χ_m , found in Landolt and Börnstein, are given in column 1. In column 2 are the limiting values deduced by Pascal (*loc. cit.*) from the additive relations in organo-metallic compounds. Column 8 gives the theoretical results calculated on the simple monatomic formula (24). Column 13 gives the results calculated according to formula (22). The equatorial components R_2 , R_3 are shown in columns 10 and 11.

Silver and gold, as might be expected, appear to be diatomic. Zinc, cadmium, and mercury show reasonable agreement when calculated as monatomic atoms. The two free valency electrons appear to lock up with a six of the W shell; $\cos \theta$ must then be equal to 1. Nitrogen and boron both having three free electrons should be calculated by the same formula. Both give values for the susceptibility which, calculated as a molecule, is near that observed. Phosphorus, arsenic, and antimony appear to tend to become monatomic. This must be connected with the fact that after phosphorus a group of six electrons can be formed. Possibly two electrons go to one atom, forming with a six an eight ring, and six remain on the other. They would then have like ordinary polar molecules, as the formula used would indicate. For the other elements, the experimental results are too variable to allow of any useful comparisons being made. Unfortunately the condition of spatial quantizing vitiates the results obtained by Pascal, as pointed out in the case of the carbon hydrogen link. Enough has been shown, however, to give confidence in the general applicability of the formulæ.

The rare gases are of great interest. The value χ_m for argon, as found by Také Soné, is the enormous magnitude of about -236×10^{-6} . Helium, according to Tänzler (*Ann. de Phys.* (4) xxiv. p. 931, 1907), must be in the neighbourhood of 44.8×10^{-6} . Calculated as rare gases from the observed susceptibilities, the Z's should be given by

$$Z(\text{He}) = \frac{2.7}{44.8} = .06$$

and

$$Z(\text{A}) = \frac{2.7 \times 9}{236} = .105.$$

The mean of these values for the effective atomic number of a rare gas is in the neighbourhood of $\frac{1}{16}$; with which speculative number we can test the theory by applying it to a paramagnetic atom with a "rare gas" valency shell.

One further example of the calculation of diamagnetism may be given. The susceptibility of water, calculated as a non-polar molecule, should be given by

$$\chi = \frac{2\{4(4 - \frac{9}{4}) - 1(1 - \frac{1}{4})\}D}{\sqrt{2}} = -11.93 \times 10^{-6}.$$

The experimental value is between -12.58 and -12.94×10^{-6} , the value decreasing as the temperature is lowered.

In order to calculate the paramagnetism in a manner which will enable comparison with experimental results, it will be necessary to derive an expression which will be independent of the applied field and the temperature. We must then substitute for the internal field H of equation (16) in terms of the precessional velocity.

If we are dealing with a molecule, our fundamental hypothesis states that q will be related with the available energy derived by the accommodation of the natural frequencies of the uncombined atoms.

This energy,

$$E_a = \Delta E_{\text{kin}} + \Delta E_{\text{pot}},$$

will be distributed in the molecule in such a way that the relation developed for the ratios of kinetic and potential energy in the magnetic field holds. This relation, already referred to, is

$$\Delta E_{\text{kin}} = -\frac{3}{2} \Delta E_{\text{pot}};$$

so we may write

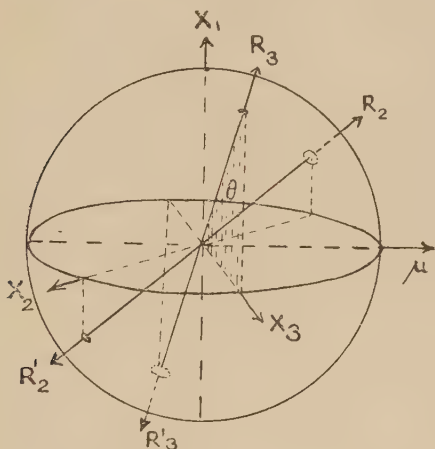
$$\Delta E_{\text{kin}} = 3E_a. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

magnetic moment as calculated by the Langevin formula $\mu = \sqrt{\frac{CR}{\overline{\cos^2 \theta}}}$, where C is the Curie constant and R the gas constant for the gram molecule, and $\overline{\cos^2 \theta} = 1/3$. The results may first be tested with the paramagnetic gases oxygen and nitric oxide.

We suppose that oxygen has two electrons belonging to each atom which remain free, the remaining eight locking up together as a W shell.

Fig. 1 represents the disposition which is assumed. The

Fig. 1.



angle θ represents the inclination of the vector normal to the orbits with the direction of μ , which, according to (10), must lie in the equatorial plane. $\cos \theta$ now has a different meaning from that which it has in the expression for diamagnetism, as can be seen by referring to our development of equations (13) and (14). The angle θ in this case we may fix by spatial quantizing, as was done by Sommerfeld. Since we are dealing with $k = 3/2$ orbits, the admissible angles will be $\cos \theta = 1/3, 2/3$, and 1, whence the average angle is given by

$$\overline{\cos \theta} = \sqrt{\frac{1}{3} \left(\frac{1}{9} + \frac{4}{9} + 1 \right)} = \sqrt{\frac{14}{27}}.$$

The probability angle, which the direction of the moment μ will make with the direction of the external field, is accounted for by the factor $\sqrt{3}$ in the Langevin formula.

In comparing results with the magneton numbers determined by Weiss and others, we therefore do not have to take it into account.

Substituting the appropriate values in (28), we thus have

$$\mu = \frac{27}{16} B \left\{ \left(1 - \frac{1}{4} \right) \left[4 \left(\frac{9}{4} - \frac{1}{4} \right) + 4 \left(\frac{9}{4} - \frac{1}{4} \right) \right] \right\} \cdot \sqrt{\frac{14}{27}} \\ = 2.699 B.$$

This figure multiplied by 5 will give the result in Weiss magnetons. We thus compare an entirely theoretical value of 13.5 with values of 13.9 and 14.2 determined by Weiss and quoted by Sommerfeld (*C. R.* clv. p. 1234, 1912 and clvii. p. 916, 1913; *Journ. de Phys.* p. 97, 1920). Our value multiplied by 5 is 13.2. The approximation of the result is satisfactory, especially as the method by which it was derived involved the hypothesis which distributes the available energy of accommodation in the molecule. It may be noted, however, that the frequency term includes a quantum number 3; *i. e.*, it refers to an activated oxygen orbit, whereas the inertial terms depend only on the unactivated principal quantum number. This does not appear an objection; it simply means that on re-distribution of energy the orbit once more assumes the value it has in its ground orbit.

Nitric oxide, which has only one free bond, should simply be half the value for oxygen with the $\sqrt{\frac{14}{27}}$ omitted. This gives 15/8 B or 9.38 Weiss. The value found is 9.2. This assumes, of course, that the accommodation energy is derived from the same element which has the free bond, otherwise the Z's would not cancel. These results, although only approximate, at least afford considerable support to the theory in its qualitative aspects. It is quite clear that under no circumstances can these molecules be other than paramagnetic.

The author takes this opportunity of expressing his indebtedness to Dr. J. W. Nicholson and Dr. N. V. Sidgwick for the interest they have shown in this and preceding papers, and to Mr. T. W. J. Taylor for the trouble he has taken in correcting proofs.

Irrigation Research Department,
Punjab University Chemical Laboratories,
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CXV. *A Note on the Photo-activation of Chlorine.* By
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THE increased chemical activity of chlorine under the influence of visible light has received much attention owing to the various photo-chemical reactions to which it gives rise, notably the synthesis of hydrogen chloride. Many attempts have been made to trace an antecedent physical change in the chlorine: Kummel and Wobig have shown that there is no dissociation †, J. J. Thomson, Lenard, and others that there is no ionization ‡, Bovie § and Wendt || that the activity ceases immediately on cutting off the light, while Mellor ¶ explained the Budde effect ** as a heating due to the reaction of the chlorine with water vapour. As a plausible assumption it may therefore be supposed that the chlorine molecule absorbs energy from the radiation (or from the secondary radiation as suggested by Weigert ††) and thereby undergoes a change of internal configuration, passing to a state of greater energy corresponding to an increase in the electronic and vibratory quantum numbers. The new state may be termed "activated," and would be characterized by a weakening of the chemical bonds, as suggested by J. J. Thomson ‡‡ and recently deduced from spectroscopic considerations by V. Henri in the cases of naphthalene §§ and sulphur |||.

The initial configuration of the molecule is governed by the quantum equation

$$E_n = \oint p \, dq = nh,$$

and the absorption obeys Bohr's frequency condition

$$h\nu = \delta E = E_m - E_n.$$

Hence no incident light can have any effect unless its frequency ν is at least sufficient to furnish the necessary

* Communicated by Prof. G. W. Todd, M.A., D.Sc.

† Kummel and Wobig, *Zeit. für Elektrochemie*, xv. p. 252.

‡ J. J. Thomson, *Proc. Camb. Phil. Soc.* xi. p. 90 (1901).

§ Bovie, *Journ. Amer. Chem. Soc.* xxxvii. p. 1721.

|| Wendt, *Journ. Amer. Chem. Soc.* xlv. p. 2377.

¶ J. W. Mellor, *Trans. Chem. Soc.* lxxxi. p. 1280 (1902).

** Richardson, *Phil. Mag.* xxxii. p. 227 (1891).

†† F. Weigert, *Zeit. Physikal. Chem.* cvi. p. 407 (1923).

‡‡ J. J. Thomson, "The Electron in Chemistry."

§§ V. Henri and De Laszlo, *Proc. Roy. Soc.* 105 A, p. 662 (1924).

||| V. Henri and Teves, 'Nature,' cxiv. p. 994 (Dec. 1924).

quota δE . If the final state E_m is not quantified, ν will then be a threshold value above which light is absorbed, and in the presence of a suitable reagent chemical action commences.

It becomes of interest, therefore, to investigate the relation between the activation, and the frequency of the illumination; quantitative work in this direction does not appear to have been published, and only recently has a similar investigation been made on the photo-dissociation of sulphur dioxide*. In the present work the photo-synthesis of HCl was used as the criterion of the activation of the chlorine, and the reaction velocity determined for different parts of the spectrum.

A modified form of the actinometer used by Burgess and Chapman† was employed. It consisted essentially of a bulb in which the gas mixture was illuminated, and having a layer of water in the lower portion to absorb any HCl formed. By means of stopcocks, it could be placed in communication either with an exit tube, or a narrow bore calibrated index tube. Any contraction in the gas volume was then measured by the movement of an indicator in the latter. The whole apparatus was made of glass, and immersed in a large water-bath to ensure temperature stability, an air thermometer being placed beside the bulb as a further check. The bath was encased in an opaque cover provided with a small window.

The gases were provided by the electrolysis of pure concentrated HCl with a current of 2 amps. and the cell used at the point of minimum oxygen adulteration according to Chapman‡. The cell was run for 40 hours to saturate all the liquid and expel atmospheric air. To decrease the effect of inhibiting agents, the incoming gases were passed through a suitably adjusted beam of white light. A very sensitive gas mixture was finally obtained.

The illumination was provided by a "Pointolite" electric arc which had the advantage of a very low percentage of accompanying heat radiation; the point source enabled the light to be brought to a focus by a lens system. This focus fell in the plane of an aperture fitted with a shutter, and having a water-cell and light filter behind the latter. The colour filters made by the Ilford Company were used, and by their means, narrow bands could be isolated from the continuous spectrum, of approximately equal width, and without

* R. A. Hall, *Trans. Faraday Soc.* xx, p. 107 (1924).

† Burgess and Chapman, *Journ. Chem. Soc.* lxxxix, 2, p. 1399 (1906).

‡ Chapman and MacMahon, *Journ. Chem. Soc.* xc, pp. 135 and 959.

any extraneous radiation whatever. After diverging from the focus, the rays passed through the window of the water-bath and fell upon a gas bulb.

In making an exposure, the water in the bulb was tested for complete chlorine saturation, and the bulb filled by allowing the gas mixture to pass through it for half an hour. All taps were then closed, and the apparatus left for half an hour in the dark to test equilibrium. The shutter was then opened, and timed readings of the indicator taken. The period of inertness was always observed, followed by the growth of the reaction velocity to a steady rate. With the most sensitive mixtures, a large Draper effect was noticed. The chief source of difficulty was found to be the retarding of the reaction by inhibiting agents present in minute quantity. A series of exposures under apparently identical conditions gave readings which varied by as much as 200 per cent. This negative catalysis has been studied by Burgess and Chapman* and the latter has also shown theoretically that the retardation is proportional to the quantity of inhibitor present†. Precautions were therefore taken of running strongly illuminated chlorine through the apparatus for a long period, and carefully standardizing the filling operations. Reaction velocities for the same conditions could then be repeated within 1 per cent. Each exposure was accompanied by a standard "control" exposure. The time-contraction readings being plotted for each light filter, the straight portions of the graphs gave by their gradients constants measuring the corresponding reaction velocities, and hence the activation of the chlorine. The limits of the spectrum bands were measured by a spectrometer; the extreme edges are given below, but margins within these limits would be ineffective owing to relative faintness. Eight filters were used covering the whole visible spectrum, but only three produced any measurable effects. With the green filter, no movement of the index could be observed over a long exposure with a pre-sensitized mixture which responded instantly to the blue-green.

The figures thus obtained do not, however, take into account the possibility that the filters might not transmit the same amounts of radiant energy. If we assume that for the same frequency the activation is proportional to the energy in the beam, then a correction could be made by reducing these reaction velocities to equivalent illumination intensities. A thermopile was therefore substituted for the bulb, and

* *Loc. cit.*

† *Loc. cit.*

connected in series with a Kelvin mirror galvanometer ; as a first approximation, the steady deflexions were taken as measures of the intensities, and used as correction factors.

| Filter. | Reaction velocity. | Range of wave-band (Angström units). | Relative light intensity. | Corrected Activated power. |
|----------------|--------------------|--------------------------------------|---------------------------|----------------------------|
| Violet | 100 | 4300-4800 | 7 | 100 |
| Blue | 27 | 4550-5000 | 11 | 17 |
| Blue-green ... | 14 | 4780-5370 | 13 | 8 |
| Green | 0 | 5050-5570 | 15 | 0 |

The activating region of the spectrum therefore corresponds to that of the general absorption of chlorine itself, *i. e.* with the continuous band extending from about 4900 Å.U. at normal temperature* and pressure† and not with the Riband fine structure bands. Activation would therefore seem in this case to be concomitant with the non-quantification of the vibratory motions.

In conclusion, I should like to express my indebtedness to the helpful criticism of Professor G. W. Todd throughout the course of this work.

CXVI. *Constancy of Total Photo-Current from Sodium with Temperature Change 20° C. to -190° C.*‡. By ROBERT C. BURT §.

IN order to obtain uncontaminated sodium surfaces, the cells used in this experiment were prepared by driving sodium electrolytically through the walls of a highly evacuated bulb ||. Much light has been thrown upon the mechanism of this remarkable phenomenon in a paper which Joffe ¶ has

* Dobbie and Fox, Proc. Roy. Soc. 99 A, p. 456.

† Narayan and Gunnaya, Phil. Mag. xlv. p. 830.

‡ Dr. H. E. Ives, Jour. of Optical Soc. of America, vol. viii. No. 4, p. 551.

§ Communicated by Prof. R. A. Millikan.

|| E. Warburg, *Wied. Ann.* xxi. p. 622 (1884); *id.*, *ibid.* xl. p. 1 (1890). A. Herz, *ibid.* liv. p. 245 (1895). W. P. Graham, *ibid.* lxiv. p. 51 (1898). C. A. Skinner, *ibid.* lxxviii. p. 754 (1899). K. Mey, *Ann. der Phys.* (4) xi. p. 130 (1903). W. Neuswanger, *Phys. Rev.* (2) vii. p. 263 (1916). For complete bibliography, see "The Electrical Conductivity of Sodium Chloride in Molten Glass" by Willard J. Sutton and Alexander Silverman, *Journal of the American Ceramic Society*, vol. vii. No. 2, February 1924, p. 102.

¶ A. Joffe, *Ann. der Physik*, lxxii. p. 461.

recently published. The method was brought to my own attention by Dr. A. W. Hull, whose kindness in performing for me such an electrolysis in his laboratory I am pleased to acknowledge. It is appropriate to describe it as electrolysis through glass.

The arrangement used in these experiments was as follows. A 40 watt incandescent lamp bulb (the well evacuated tungsten filament lamp in most common use today) was immersed, stem up, in a molten salt or salt and water solution containing sodium ions, and a potential of about 100 volts was applied between the lighted filament and the solution surrounding the lower part of the bulb. The bulb itself is of soda glass—an essential condition. The vacuum, rendered conducting by electrons from the filament, is, so to speak, electroplated by the sodium which passes from the solution anode through the glass electrolyte.

Since a larger electrolytic current can be sent through the glass if it is hot, I have used in place of a water solution molten sodium nitrate, which melts at 312°C . This is well below the baking-out temperature which had previously been maintained for more than 24 hours. At the temperature of 312°C . the sodium evaporates and condenses at the top-inside of the bulb above the level of the hot surrounding sodium nitrate. However, it can be redistilled into the bottom when it is once inside. The filament when not lighted is used as a collector for the photo-electrons. By keeping it heated during the redistillation no sodium can condense upon it. During redistillation the pressure of sodium vapour must not become too high else a sodium arc will form and burn out the filament. Currents as large as 0.2 ampere have been used for this electrolysis; larger currents are likely to burn out the filament. Control of the electrolytic current is obtained by adjusting the temperature of the filament.

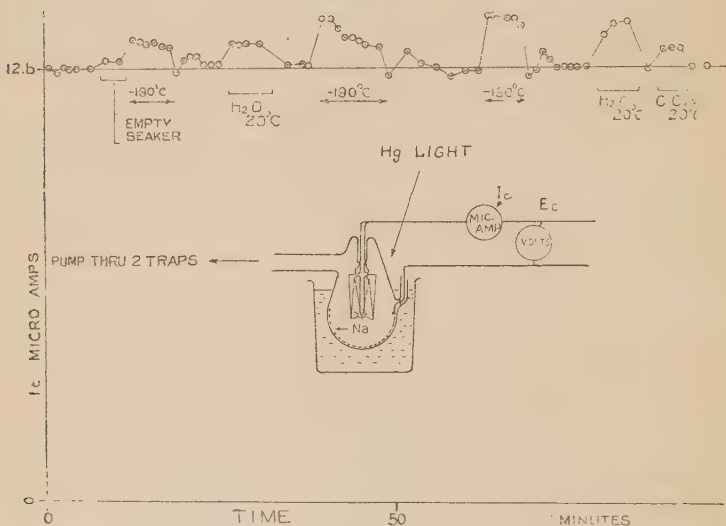
It was found that the vacuum inside cells which had been sealed off the pumps was not sufficiently perfect to keep the sodium surface clean, even with the use of charcoal side tubes. For this reason the results reported here were obtained with cells which were attached to the mercury pumps, although results similar to those given here on contaminated surfaces were obtained in cells which had been sealed off.

In the centre of fig. 1 is shown the cell which is connected through two liquid-air traps to two diffusion pumps. Light is incident from above on the sodium surface at the bottom of the bulb. With a constant potential (measured by a Weston model 45 voltmeter) on the collector the total

photocurrent is measured (by means of a Rawson unipivot millimeter, type 501) while the illumination is held constant.

At the top of fig. 1 have been plotted photo-currents against time. Under the influence of the light the photo-current was constant at 12.6 micro-amperes. But when the empty beaker was put in place about the cell there was a small increase in the current as shown, and when liquid air was put in the beaker there was a greater increase. The photo-current decreased as the liquid air evaporated. When the air was removed, the current returned to 12.6,

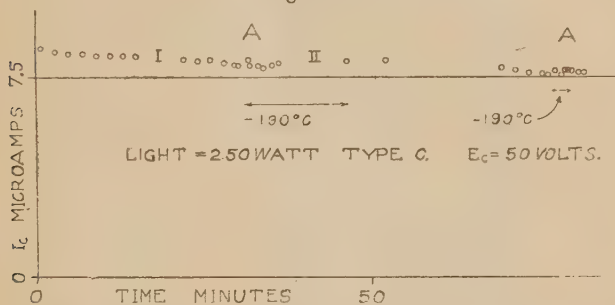
Fig. 1.



and when water was placed in the beaker, the current increased to the value shown by the second maximum. A full beaker of liquid air gave the third maximum, but the current returned to its original value when the air was removed; when again dipped in air, the fourth prominent maximum was obtained. With water at room temperature the next maximum was found. A beaker of carbon tetrachloride raised about the cell gave the last maximum. The variation when the liquid air is removed is due probably to fog or mist in the air and on the glass immediately after the removal of liquid air. The constancy of total current at 12.6×10^{-6} ampere from this cell at room temperature over such a long period as that shown on the curve when the cell is subjected to such intense light as required to give this current is, I think, worthy of note.

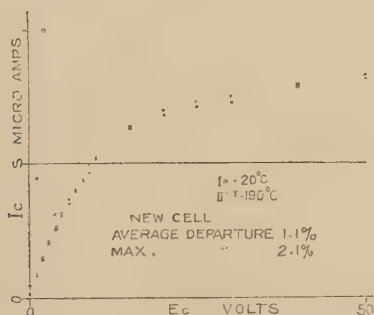
The foregoing experiments were thought to be good evidence that the increases were due to scattered light from the liquid and beaker. To test this more thoroughly, blackening the bulb with paint, lamp-black, and other things was tried. Cracked cells and cracked paint were the usual results, but finally a cell with the bottom wrapped in black paper gave the results shown in fig. 2.

Fig. 2.



The light used in this case was a 250 watt stereopticon lamp. Fig. 2 shows current plotted against time. The cell was at room temperature except for the time embraced by the double arrows. It will be seen from a glance at the points marked A that when the bulb was immersed in liquid air no appreciable change in the value of the photo-current resulted. This seems to show quite conclusively that if there

Fig. 3.



is any temperature effect upon the photo-sensitiveness of sodium between liquid air and room temperature, it must be an extremely small one.

During the time-intervals indicated in fig. 2 by I and II two complete photo-current potential curves were taken. These curves are shown in fig. 3, the dots representing the

curve taken at 20°C . and the arrowheads that at -190°C . It will be seen that the two curves are everywhere practically coincident, though there are four points which show a systematic difference all in the same direction. The actual readings in the case of both curves are shown in Table I.

TABLE I.

| Voltage. | Photo-current. Room Temp. | Photo-current at -190°C . |
|----------|------------------------------|----------------------------------------------|
| E_c . | I_{20} . | I_{-190} . |
| 50 | 8.25 | 8.20 |
| 40 | 7.80 | 7.82 |
| 30 | 7.35 | 7.44 |
| 25 | 7.10 | 7.26 |
| 20 | 6.80 | 6.95 |
| 15 | 6.37 | 6.31 |
| 10 | 5.10 | 5.20 |
| 9 | 4.70 | 4.84 |
| 8 | 4.38 | 4.40 |
| 7 | 3.97 | 3.99 |
| 6 | 3.52 | 3.56 |
| 5 | 3.06 | 3.10 |
| 4 | 2.60 | 2.62 |
| 3 | 2.07 | 2.10 |
| 2 | 1.48 | |
| 1 | .88 | .80 |
| 0 | .20 | .28 |

These observations are taken in the same way as those recently published by H. E. Ives, but fail to show any such variations with temperature as he found.

Fig. 4 is a continuation of the photo-current time curve begun in fig. 2. At the time marked "Air off 2nd trap" the pump was disconnected from the system by a mercury cut-off close to the pump, and at the same time the liquid air was removed from that one of the two liquid-air traps in series which was nearest to the bulb and which had been cooled a considerable time after the first liquid-air trap had been functioning. The object of removing this liquid-air trap was to allow a very minute amount of impurity to flow back into the bulb. The effect of this impurity was observed instantly by an increase in current as shown by the arrow in fig. 4 above the comment "Air off 2nd trap." A voltage-current curve was taken at III, and then the cell was cooled in liquid air and a large increase in total current occurred; another voltage-current curve was taken at IV.

Fig. 4.

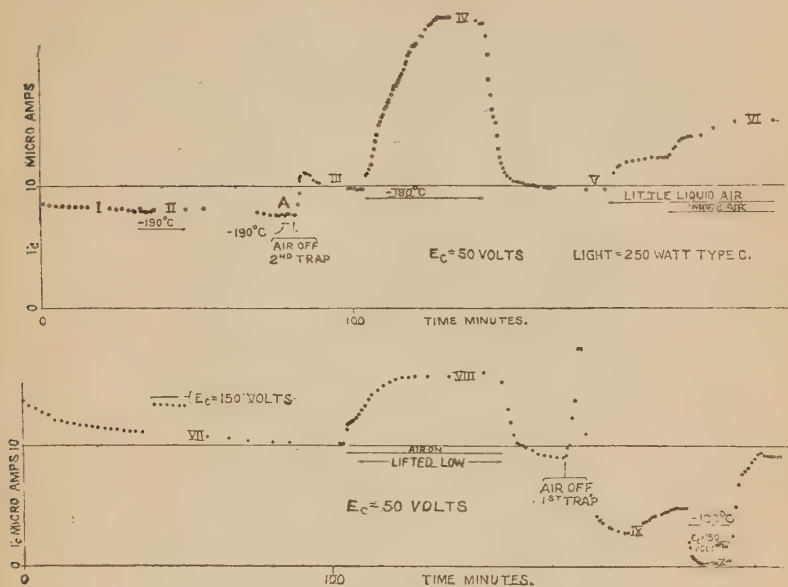
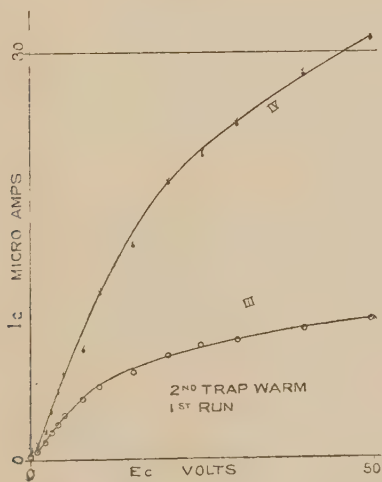


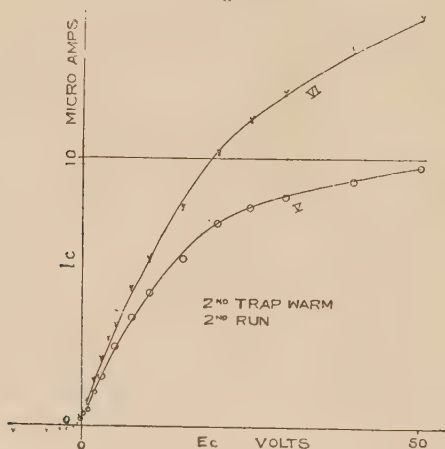
Fig. 5.



These last two are shown in fig. 5. Liquid air was then removed and other similar curves were taken at V and VI.

and they are plotted in fig. 6. The same current-time curve, taken the following day, is continued at the bottom of fig. 4. Voltage-current curves were taken at VII and VIII, the first at room, the latter at liquid air temperature. These last two curves are not reproduced since they were practically identical with V and VI.

Fig. 6.



At the point marked "Air off 1st trap," the liquid air was removed from the trap nearest the pump. This was the first trap to be cooled during evacuation, and hence contained much more condensed vapour. With illumination and the collector voltage constant, the photo-current at first doubled, then dropped to about one-third its former value, as shown in fig. 4. When it was believed constant at IX, another voltage-current curve was taken. Next it was cooled in liquid air, and this time a decided drop in the total current occurred. At X a voltage-current curve was again taken (fig. 7). Removal of the liquid air caused an increase in total current. Further experimenting on this cell was prevented by a crack which developed at this point in the bulb.

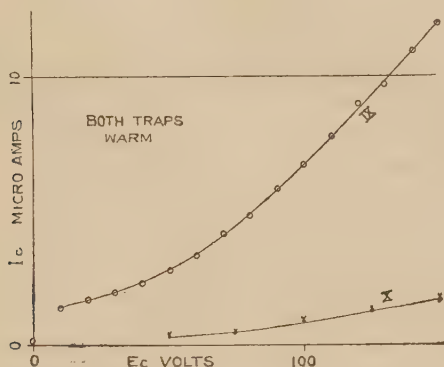
The question as to whether there may be minute traces of impurities in the sodium within the bulb of the sort not dependent upon residual gases or vapours has no bearing upon the main conclusion which is drawn below. For the sake, however, of obtaining evidence as to the possible existence of impurities coming through or out of the glass the following tests were made:—

1. An effort was made to drive both potassium and lithium through this glass without any success whatever.

2. A bulb of this kind was used as a sodium voltameter, and the correct atomic weight of sodium to one part in 500 was obtained. This limit of accuracy was set in this experiment simply by the uncertainty in the measurement of the quantity of electricity producing the deposit of sodium.

3. A sodium arc was formed in the bulb, and no trace of lines other than sodium obtained. The last test presumably means a purity of at least one part in 500,000.

Fig. 7.



Dr. Ives appears to find a temperature effect upon photo-currents from both sodium and potassium between these temperature limits. In the foregoing experiments it appears that when the utmost precautions are taken against contamination no temperature effect on photo emission from sodium is found. By contaminating the surface, however, both of the types of temperature effects which Dr. Ives obtains, namely, an increase in one case and a decrease in another, are found.

It is believed that the above evidence is convincing that :

(1) *The total photo-current of sodium is constant, within a few per cent. at most, over a temperature range 20° to -190° C., if the surface is sufficiently pure;*

(2) *if the surface is just slightly contaminated, it may be much more sensitive at low temperature than at room temperature; and*

(3) *if slightly more contaminated by some unknown vapour, the surface may be several times less sensitive at liquid air temperature than at room temperature.*

That the change of total photo-electric current within the temperature limits noted should be less than 1 per cent. for a pure surface is supported by some theoretical work of

Dr. J. R. Nielsen in this laboratory. This work has been submitted for publication in the *Physical Review*.

I wish to acknowledge with thanks the suggestions, advice, counsel, and inspiration of the Director of this Laboratory, Professor Robert A. Millikan.

Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California.

October 30, 1924.

CXVII. *The Broadening of Lines in Arc Spectra and the Stark Effect.* By H. LOWERY, M.Sc. (Lond.), A.Inst.P., F.R.A.S., Assistant Lecturer in Physics, Manchester University*.

[Plate XII.]

Introduction.

IN a very interesting paper † on "The Broadening of Spectral Lines caused by Increased Current Density and their Stark Effects," Kimura and Nakamura give results of experiments on the broadening of lines in the arc spectra of copper, silver, gold, magnesium, calcium, chromium, and nickel produced by heavy currents of the order 40 amperes and upwards. The nature of the broadening is compared with the displacement and separation of the lines into components by a strong electric field (Stark effect), the results of the work on the Stark effect by Stark and Kirschbaum ‡, Anderson §, Takamine ||, Howell ¶, Takamine and Kokubu **, and Yoshida †† being used for this purpose.

The general conclusion arrived at from this comparison was that "the lines showing the Stark effect were generally broadened easily in the spectrum of a heavy current arc The lines showing displacements towards the red side in the Stark effect broadened on the red side when the current density was greatly increased in the arc Similarly, the lines showing displacement towards the violet side in the Stark effect broadened on the violet side. The

* Communicated by Prof. W. L. Bragg, F.R.S.

† Jap. Jour. of Phys. ii. No. 3-5, p. 61 (1923).

‡ *Ann. d. Phys.* xliii. p. 1030 (1914).

§ *Astrophys. Jour.* xlv. p. 104 (1917).

|| *Astrophys. Jour.* l. p. 27 (1919).

¶ *Astrophys. Jour.* xlv. p. 87 (1916).

** *Mem. Coll. Sci. Kyoto Imp. Univ.* iii. p. 173 (1918).

†† *Mem. Coll. Sci. Kyoto Imp. Univ.* iii. p. 287 (1918).

lines having isolated components generally developed broadened lines at the position of such components."

In a previous paper* the present writer has described experiments in which spectroscopic observations were made upon the interrupted silver, gold, and copper arcs, using the method adopted by Hemsalech and de Gramont† in their study of the occurrence of enhanced lines in the arc. The experiments were originally begun with the object of investigating the existence of the Stark effect in the arc and, in the paper referred to, attention was drawn to the widening of the lines in the arc spectrum of silver in the region near the fixed pole where presumably the electric fields are very intense during the early stages of the arc flash.

In view of the distinct broadening of lines in arc spectra produced under two apparently different sets of conditions, viz. : (1) those due to a heavy current (voltage 110 volts) as in the experiments of Kimura and Nakamura, and (2) those obtaining in the interrupted arc, it will be of interest to compare the nature of the broadening in the two cases and to consider the results in connexion with the Stark effect.

Experimental Results.

The *interrupted* arc spectra of silver, gold, copper, nickel, and iron were investigated. Kimura and Nakamura give results of their experiments for all these metals except iron. The nature of the broadening in the experiments with the interrupted copper, silver, and gold arcs is given in the following tables (I, II, and III). Symmetrical broadening is indicated by vr or VR. The symbols vR, Vr, v, r, V, R denote the different kinds of unsymmetrical broadening respectively, a single letter indicating broadening on one side only. The large and small letters are employed to show in a general way the relative sizes of the wings. The extent of any wing from the original line is usually of the order 1 to 5 Å.U., but accurate determinations of the size of the wings are not possible owing to their diffuse edges. Intensities range from 0 (weakest) to 10 (strongest).

The last column in the tables indicates the nature of the broadening obtained by Kimura and Nakamura in their experiments.

* Phil. Mag. xlviii. p. 1122 (Dec. 1924).

† Phil. Mag. xliii. (Feb. and May 1922).

TABLE I.—Copper.

| Series formula. | Wave-lengths in I.A. | Nature of broadening (interrupted arc). | Intensity (interrupted arc). | Nature of broadening (Kimura and Nakamura). |
|-------------------|----------------------|-----------------------------------------|------------------------------|---------------------------------------------|
| $1\pi_2-4\delta'$ | 3654.3 | vr | 6 | Wing on red side. |
| $1\pi_2-4\sigma$ | 3825.05 | v | 2 | Feeble intensity. Broadening not recorded. |
| $1\pi_1-4\sigma$ | 3861.75 | v | 2 | Feeble intensity. Broadening not recorded. |
| | 3894.49 | vr | 1 | Feeble intensity. Broadening not recorded. |
| $1\pi_2-3\phi$ | 4015.8 | v | 1 | One sided (violet) wing. |
| $1\pi_2-3\delta'$ | 4022.67 | vR | 10 | Red (bright) & violet (faint) wings. |
| $1\pi_1-3\phi$ | 4056.7 | V | 4 | One-sided (violet) wing. |
| $1\pi_1-3\delta$ | 4062.69 | vR | 10 | Red (strong) & violet (faint) wings. |
| $1\pi_1-3\delta'$ | 4063.30 | (v?) r | 2 | Red (strong) & violet (faint) wings. |
| $1\pi_2-3\sigma$ | 4480.38 | R | 9 | Not recorded. |
| $1\pi_1-3\sigma$ | 4530.84 | R | 10 | " " |
| $1\pi_2-2\delta'$ | 5153.23 | V | 10 | " " |
| $1\pi_1-2\delta$ | 5218.17 | V | 10 | " " |

Note on Table I.—Copper.

It is assumed that the line $\lambda 4062.69$ (I.A.) of intensity 10 is identical with the line $\lambda 4062.14$ of Takamine and of Kimura and Nakamura.

Note on Table II.—Silver.

$\lambda\lambda 4210.71, 4212.60$. In describing the broadening of these two lines in their experiments, Kimura and Nakamura say, "The images of these lines presented an appearance similar to the self-reversal of a single spectral line, the violet components of the former line and its red component together with the corresponding one of the latter forming wings on both sides."

In the interrupted arc the space between the two lines at the beginning of the flash is hazy, and might be regarded as

TABLE II.—Silver.

| Series formula. | Wave-length in I.A. | Nature of broadening (interrupted arc). | Intensity (interrupted arc). | Nature of broadening (Kimura and Nakamura). |
|-------------------|---------------------|-----------------------------------------|------------------------------|----------------------------------------------|
| $1\pi_2-4\delta'$ | 3682.30 | vr | 5 | Bright violet and faint red wings. |
| $1\pi_1-4\delta$ | 3810.71 | vr | 5 | Bright violet and faint red wings. |
| $1\pi_1-3\sigma$ | 3981.72 | r | 6 | One-sided (red) wing. |
| $1\pi_2-3\delta'$ | 4055.81 | VR | 10 | Broad red wing and diffuse violet component. |
| $1\pi_1-3\delta$ | 4210.71 | Vr | 10 | (See note below). |
| $1\pi_1-3\delta'$ | 4212.60 | vR | 10 | " " |
| | 4226.39 | r | 5 | Faint shading on red side. |
| $1\pi_2-3\sigma$ | 4476.12 | r | 8 | Slight broadening on red side. |
| $1\pi_1-3\sigma$ | 4668.52 | r | 8 | Not recorded. |

filled with a wing on the red side of λ 4210.71, or with a wing on the violet side of λ 4212.60, or even with two such wings either superimposed or meeting each other at their edges.

TABLE III.—Gold.

| Wave-length in I.A. | Nature of broadening (interrupted arc). | Intensity (interrupted arc). | Nature of broadening (Kimura and Nakamura). |
|---------------------|-----------------------------------------|------------------------------|---------------------------------------------|
| 3796.00 | Vr | 8 | Broadening toward violet side. |
| 4084.14 | r | 8 | Slight broadening toward the red. |
| 4128.65 | r | 4 | Faint, but slightly diffuse both sides. |

In the above tables the broadening in the interrupted arc spectra is given only for those lines on which the Stark effect has been observed, though many other lines, in the case of each metal, exhibited traces of broadening at the beginning of an arc flash. The copper lines $\lambda\lambda$ 3687, 3689, 3830, and the silver lines $\lambda\lambda$ 3841, 4081, 4207 (on all of which the Stark effect has been observed), were so feeble in all the photographs that no definite statement can be made with regard to their possible broadening.

Comparison and Discussion of Results.

The above tables show that the broadening of lines in the interrupted arc spectra at the beginning of an arc flash is practically of the same nature as Kimura and Nakamura obtained in their experiments with the steady arc. The broadening of the following lines is not given by Kimura and Nakamura, the first three lines being very faint in their plates, the remainder falling outside the region of their investigation:—Copper: $\lambda\lambda$ 3825, 3862, 3895, 4480, 4530, 5153, 5218; Silver: λ 4668. The broadening of all these lines in the interrupted arc is given in the above tables and, with the slight exception of λ 3895 (copper), agrees with the expected broadening from considerations of the Stark effect.

In order to illustrate more fully the nature of the comparison between the broadening of the lines and their Stark effects, a portion of Takamine's table on the Stark effect for copper is given, together with the broadening effect under the interrupted arc conditions, where it will be seen that there is a general good agreement between the results. The positive and negative signs in the second and fourth columns refer to the components on the red and violet sides of the lines in question.

TABLE IV.—Copper.

| λ (I.A.). | <i>p</i> -comp. | | <i>n</i> -comp. | | Broadening (inter- rupted arc). | Intensity. |
|----------------------|-------------------|------------|-------------------|------------|------------------------------------------|------------|
| | $\Delta\lambda$. | Intensity. | $\Delta\lambda$. | Intensity. | | |
| 3825.05 | −0.16 | 3 | −0.10 | 3 | v | 2 |
| 3861.75 | −0.11 | 3 | −0.12 | 3 | v | 2 |
| 3894.49 | +0.27 | 1 | +0.23 | 1 | vr | 1 |
| 4015.8 | −0.47 | 2 | −0.43 | 2 | v | 1 |
| 4022.67 | +0.46 | 7 | +0.33 | 7 | vR | 10 |
| 4956.7 | −0.62 | 3 | −0.6. | 3 | V | 4 |
| 4062.69 | +0.60 | 10 | +0.44 | 10 | vR | 10 |
| 4063.30 | +0.37 | 4 | +0.33 | 4 | (v?) r | 2 |
| 4480.38 | +0.09 | 6 | +0.11 | 6 | R | 9 |
| 4530.84 | +0.04 | 6 | +0.03 | 6 | R | 10 |
| 5153.23 | −0.10 | 6 | −0.05 | 6 | V | 10 |
| 5218.17 | −0.09 | 10 | −0.07 | 10 | V | 10 |

It may be noted further that, at least in the interrupted

arc experiments, without exception the lines of the diffuse series are broadened to a greater extent than those of the principal and sharp series. In addition, as in Takamine's work, the lines of the diffuse series for silver are affected on both sides, thus differentiating these lines from those of the sharp series which are affected on one side only.

Nickel and Iron.

Kimura and Nakamura examined the nickel arc under a heavy current but did not find any well-marked broadening of lines as in the case of copper, silver, and gold, though such broadening would be expected as many nickel lines show the Stark effect*. In the *interrupted* arc spectra, any broadening which existed was of such a small order that no definite statement of its nature can be given. Iron was also one of the metals examined in the interrupted arc and the results were as in the case of nickel. It may be noted here that Takamine states that the Stark effect for iron is exceedingly small compared with that for other elements.

Magnesium.

Probably the most striking agreement between the results obtained by Kimura and Nakamura and those of the interrupted arc experiments is to be found in the metal magnesium. The interrupted arc spectrum of this metal was studied by Hemsalech and de Gramont† during their research on the occurrence of enhanced lines in the arc. They give a photograph (plate xviii. *loc. cit.*) of the interrupted magnesium arc spectrum over a region including the lines $\lambda\lambda$ 4352, 4571, 4703, which shows the first and third lines with well-marked wings developed on the red side as in the experiments of Kimura and Nakamura. Though the second line λ 4571 is displaced to the red in the Stark effect, it appears fairly sharp on the photographs of the heavy current arc. The photograph of Hemsalech and de Gramont referred to above shows this same line quite sharp in the interrupted arc!

In view of the close connexion which the above experimental results seem to indicate between the broadening of lines in the arc spectra and the Stark effect, it is interesting to review Duffield's‡ experiments on the effects of pressure

* Takamine, *Astrophys. Jour.* l. p. 33 (1919).

† *Phil. Mag.* xliii. (May 1922).

‡ *Phil. Trans.* A. ccix. p. 205 (1908); ccxi. p. 33 (1911).

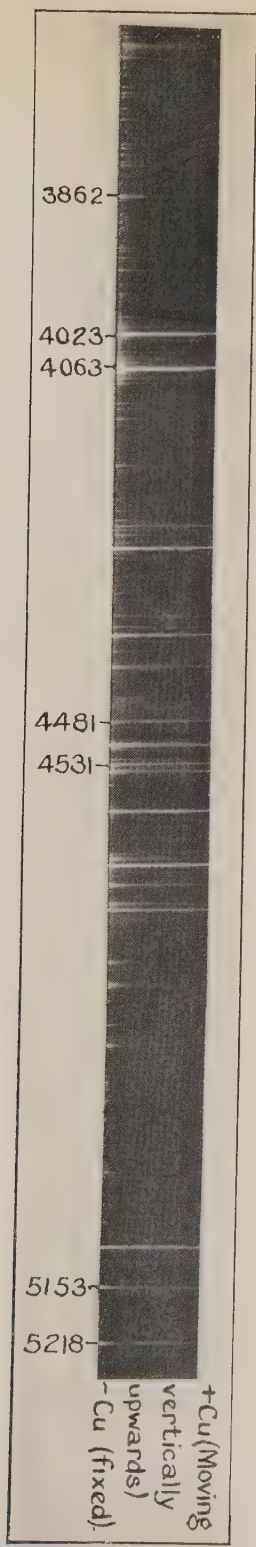
on arc spectra when the principal effect noted was a broadening of many of the lines. Duffield records that at high pressures the metal arcs he examined were frequently blown out by the luminous metallic vapour which they expelled, so that "a single exposure was the integrated effect of a number of short-lived arcs." The spectra obtained were therefore those of interrupted metal arcs under high pressures, and the broadening effect observed in the spectra was the net result of conditions similar to those referred to above in addition to those of the high pressures employed. Duffield recognized that effects might possibly be produced in the spectra of the metal arcs under high pressure owing to the necessity for frequently bringing the poles into contact to strike the arc, for he says: "In the experiments with the iron arc the chief variables were the current strength and the length of the arc, which, on account of the necessity for continually striking the arc, could not be kept constant. The variables dependent upon these are the temperature, potential gradient, the quantity, and perhaps the density of the material in the arc."

The facts brought out by the experiments with the interrupted arc prove conclusively that the effects due to the striking of the arcs cannot be neglected in considering Duffield's results. Further, in the light of the results given by Kimura and Nakamura, since the current in the steady metal arcs of Duffield sometimes reached the value of 20 amperes, it is highly probable that the effect of such a high current density in these arcs cannot wholly be neglected in interpreting the broadening of lines in Duffield's photographs.

Finally, in connexion with the Stark effect interpretation of the broadening of lines in arc spectra, it may be pointed out that Nagaoka and Sugiura* have developed a method of observing the Stark effect by means of the arc which is more convenient than the original method involving the use of a vacuum tube. They used a special device to keep the arc steady in the vertical position. The lines originating in the lower electrode extending from the visible part of the spectrum down to the ultra-violet showed distinct separation which was identical with the Stark effect observed with vacuum tubes. It was found convenient to work with a 500 volts arc, though the effect can be observed at 100 volts.

* 'Nature,' cxi. p. 431 (1923).

Interrupted Arc Spectrum of Copper.



Explanation of Plate.

The photograph is reproduced from one of the negatives obtained when arc flashes were made between copper poles in oxygen at 350 volts and initial current 5 amperes, the lower fixed pole being negative.

Summary.

1. Attention is drawn to the similarity of the broadening of lines as produced (1) in the interrupted arc spectra of copper, silver, gold, nickel, and magnesium, (2) in the heavy current arc spectra of Kimura and Nakamura.

2. The broadening is such as would be expected from observations on the Stark effect.

3. It is pointed out that, in interpreting the broadening of lines obtained by Duffield in his experiments on the effect of pressure on arc spectra, it is necessary to take into account the effects due to the heavy currents he employed and the necessity for repeatedly striking the arc.

Again I desire to express my thanks to Dr. G. A. Hemsalech for his helpful advice while the experiments on the interrupted arc were in progress, and also to Professor W. L. Bragg, F.R.S., for his encouragement during the research.

Physics Dept.,
The University of Manchester,
Jan. 1925.

[*Note.*—A comprehensive account of the experiments and results of Nagaoka and Sugiura, mentioned above, is to be found in the *Japanese Journal of Physics*, vol. iii. Nos. 1-3, 1924.]

CXVIII. *On the Stabilization of Instable Equilibrium by means of Gyroscopic Forces*—II. By Dr. H. J. E. BETH (*Deventer*) *.

IN a preceding paper† I have proved that for the case of an even number of irrotational instabilities the equilibrium of a system with an arbitrary number of degrees of freedom may be converted into a stable one by the means of gyroscopic forces. In the present paper I wish to show

* Communicated by the Author.

† *Phil. Mag.* February 1925.

how the subject may be investigated more in detail for the cases of a mechanism with three or four degrees of freedom with the help of geometrical considerations.

Three degrees of freedom.

If in the determinantal equation

$$\Delta \equiv \begin{vmatrix} m^2 + a_{11} & g_{12}m & g_{13}m \\ -g_{12}m & m^2 + a_{22} & g_{23}m \\ -g_{13}m & -g_{23}m & m^2 + a_{33} \end{vmatrix} = 0,$$

we write

$$P = \sqrt[3]{a_{11}a_{22}a_{33}}, \quad u = \frac{m^2}{\sqrt[3]{a_{11}a_{22}a_{33}}};$$

$$X = \frac{\Sigma a_{11} + \Sigma g_{23}^2}{P}, \quad Y = \frac{\Sigma a_{22}a_{33} + \Sigma a_{11}g_{23}^2}{P^2};$$

it passes into

$$u^3 + Xu^2 + Yu + 1 = 0. \quad (1)$$

As we have supposed that the system has an even number of irrotational instabilities, we may suppose a_{11} and a_{22} to be negative, a_{33} positive. We ask how the gyroscopic force must be chosen in order to make the roots of (1) negative.

We first investigate the influence of the coefficients g_{23} , g_{31} , and g_{12} on the nature and the sign of the roots of (1). With this aim, we associate the equations (1) with the points of a plane determined by their rectangular coordinates. As the roots of (1) never become zero or infinite, a change of sign of the roots occurs only when we pass twice the locus δ of the points (X, Y) , for which (1) has equal roots.

This locus δ , represented by the equation

$$\delta \equiv X^2Y^2 - 4X^3 - 4Y^3 + 18XY - 27 = 0, \quad (2)$$

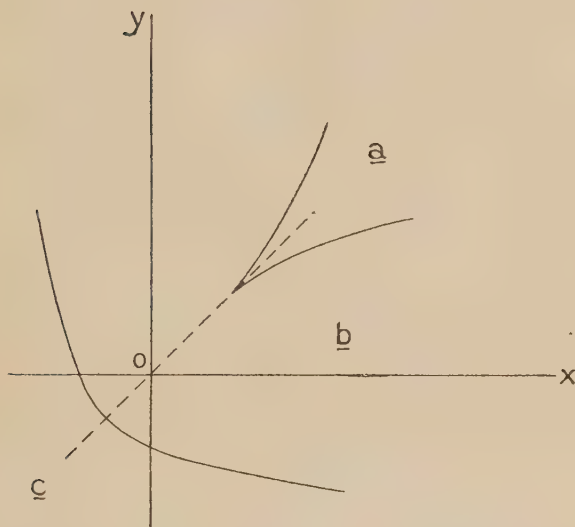
has been drawn in fig. 1. It divides the plane in three regions, viz. the region a of three negative roots, the region b of one negative and two imaginary roots, and the region c with one negative and two positive roots.

The equation (1) represents a system of straight lines containing a parameter u ; $-u$ is the parameter of direction of such a line; δ is the envelope of the system. Through any point of the plane three tangents at δ pass. For a point in a the three tangents have a positive slope; for a point in b there is only one real tangent which has a positive slope; for a point in c there are two tangents with negative and one with positive slopes.

a is the region of the stable positions of equilibrium. The irrotational equilibrium being instable, its image-point in the XY -plane is a point $Q_{irr.}(X_0, Y_0)$ in c , and

$$X_0 = \frac{\Sigma a_{11}}{P}, \quad Y_0 = \frac{\Sigma a_{11}a_{22}}{P^2}.$$

Fig. 1.



By the means of gyroscopic forces, the position of equilibrium passes into

$$X = X_0 + \frac{\Sigma g_{23}^2}{P}, \quad Y = Y_0 + \frac{\Sigma a_{11} \cdot g_{23}^2}{P^2} \dots \dots (3)$$

The image-point moves in the direction :

$$\lambda = \frac{Y - Y_0}{X - X_0} = \frac{1}{P} \frac{\Sigma a_{11} g_{23}^2}{\Sigma g_{23}^2} = \frac{\Sigma -u_{10} g_{23}^2}{\Sigma g_{23}^2}, \quad \dots (4)$$

where u_{10} , u_{20} , and u_{30} are the roots u corresponding with the point $Q_{irr.}$

From this it follows that the directions in which the image-point may move by reason of the gyroscopic force are limited by those two magnitudes of $-u_{10}$, $-u_{20}$, and $-u_{30}$, which include the third, and that any direction within

the angle determined by the two corresponding tangents at δ is a possible one.

We therefore draw from $Q_{\text{irr.}}$ at δ the two tangents having the greatest and the smallest coefficient of direction. Of the tangents we take the half-lines with positive X -components (according to (3) $X - X_0$ is always positive). The angle within these two half-lines contains all image-points which may be reached by the means of gyroscopic forces. The result may be stated in still simpler terms: we draw from $Q_{\text{irr.}}$ the tangent at the border of region a ; *the part of a below this tangent contains the points we may reach.*

From this we conclude again that it is always possible to stabilitate the two irrotational instabilities; moreover, we observe that from fig. 1 it follows at once that by means of gyroscopic forces stability may never be disturbed (when the irrotational equilibrium is stable, its image-point is in a and the angle between the limiting tangents is also entirely within a).

Returning to the case of instable irrotational equilibrium, we have still two different cases to consider, viz. 1° $Q_{\text{irr.}}$ is below the line $Y = X$, 2° $Q_{\text{irr.}}$ is above the line $Y = X$. In the second case the part of region a we may reach consists of two different parts, α' and α'' , of different character. When in this case a direction of motion for the image-point is given in order to enter into a it will for the first time enter into a in a point of α' , but it will leave the region a again and enter into it for the second time in a point of α'' . We will neglect the part α' and occupy ourselves only with α'' . We therefore speak only of stabilization by the means of gyroscopic forces when the equilibrium remains stable as long as the angular velocity of the flywheels is beyond a minimum value (figs. 2 *a* and 2 *b*).

If ξ , η , and ζ are the principal coordinates of the mechanical system, we may introduce a representative point of which the rectangular coordinates are ξ , η , and ζ . The components of the gyroscopic force along the axes are given by

$$K_{\xi} = -g_{12}\dot{\eta} + g_{13}\dot{\zeta},$$

$$K_{\eta} = -g_{23}\dot{\zeta} + g_{12}\dot{\xi},$$

$$K_{\zeta} = -g_{13}\dot{\xi} + g_{23}\dot{\eta}.$$

The gyroscopic force is the vector-product of the velocity of the representative point and the vector G , of which the ξ -, η -, and ζ -components are g_{23} , g_{31} , and g_{12} .

Fig. 2 a.

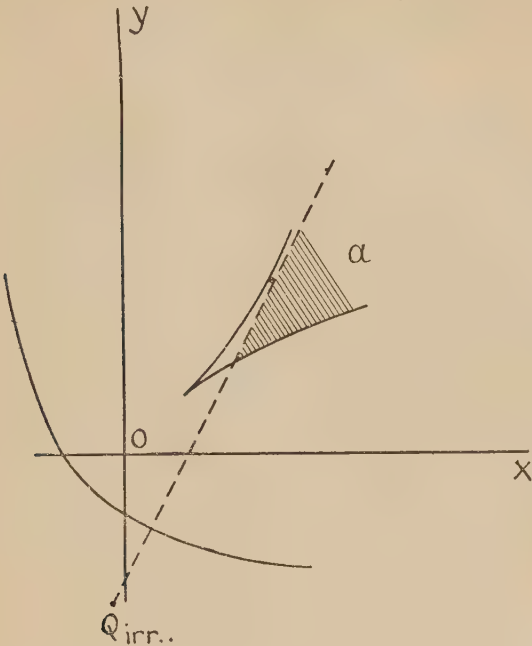
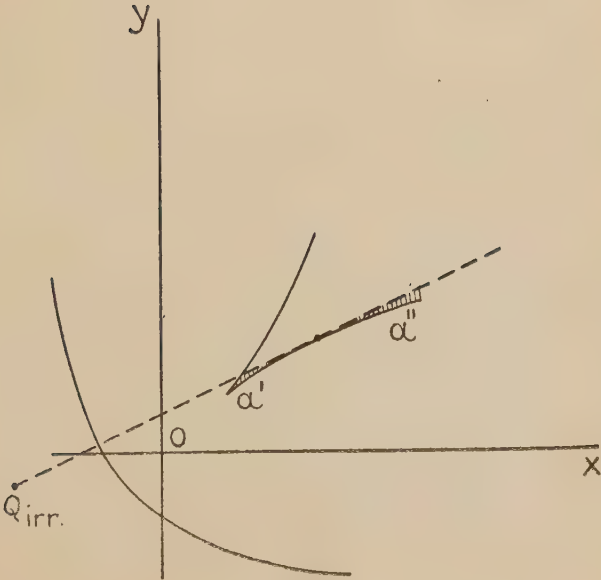


Fig. 2 b.



We first consider this vector $G(g_{23}, g_{31}, g_{12})$. Its direction in space is not determined by the direction of motion

$$\lambda = \frac{Y - Y_0}{X - X_0}$$

in the plane of δ . From (4) we deduce that the direction of G belonging to a given λ is an arbitrary generatrix of the quadratic cone

$$\lambda(\xi^2 + \eta^2 + \zeta^2) + (u_{10}\xi^2 + u_{20}\eta^2 + u_{30}\zeta^2) = 0,$$

or

$$(\lambda + u_{10})\xi^2 + (\lambda + u_{20})\eta^2 + (\lambda + u_{30})\zeta^2 = 0.$$

We suppose u_{30} to be the negative root for $Q_{\text{irr.}}$. Then the directions λ that may bring the image-point in the XY -plane into the region of stability a are between the limits $-u_{30}$ and zero (when $P_{\text{irr.}}$ is above the line $Y=X$, we consider only the part a'').

For $\lambda = -u_3$ the cone has contracted into the ζ -axis (axis of stability). All cones of the pencil for $0 < \lambda \leq -u_{30}$ have their real axis along the ζ -axis, do not intersect each other, and fill up the space within the cone V :

$$u_{10}\xi^2 + u_{20}\eta^2 + u_{30}\zeta^2 = 0,$$

or

$$V \equiv a_{11}\xi^2 + a_{22}\eta^2 + a_{33}\zeta^2 = 0,$$

where V represents the potential function of the positional forces. Any line passing through O and at the inside of V represents a possible position of the vector $G(g_{23}, g_{31}, g_{12})$; the generatrices G of a similar cone of the pencil correspond to a similar direction λ in the plane of δ .

The magnitude of G is given by (3),

$$\sqrt{(\Sigma g_{23}^2)} = \sqrt{\frac{1}{P}}(X - X_0).$$

As P is a constant (for the same irrotational equilibrium), the magnitude of the vector G is proportional to the square root of the X -component of the displacement in the plane of δ . With the help of fig. 2 (or by the solution of a biquadratic equation) we are able to find the minimal value of G with any possible direction λ ; the minimum minimorum we have for $\lambda = -u_{30}$, for which value of λ G has the ζ -direction.

We now proceed to the gyroscopic force F itself. As G is a fixed line during the motion, the force F remains parallel with a fixed plane U normal to G . From the

possible directions of G we deduce that all planes U are possible which have with the supplementary cone C' of cone V :

$$C' \equiv \frac{\xi^2}{a_{11}} + \frac{\eta^2}{a_{22}} + \frac{\zeta^2}{a_{33}} = 0$$

an elliptical intersection. With any possible plane U is associated a value of λ . When the motion of the representative point is projected on a plane U , the gyroscopic force in any point is normal to the velocity of the projection and equal to the product of this velocity and a constant factor G which has for any plane U a minimum value. This constant has the smallest value if U is the plane of the instabilities.

Four degrees of freedom.

For this case the determinantal equation $\Delta=0$ has the form

$$u^4 + Xu^3 + Yu^2 + Zu + 1 = 0, \quad . \quad . \quad . \quad (5)$$

where

$$P = \sqrt[4]{a_{11}a_{22}a_{33}a_{44}}, \quad u = \frac{m^2}{P}.$$

$$X = \frac{\Sigma a_{11}}{P} + \frac{\Sigma g_{12}^2}{P^2},$$

$$Y = \frac{\Sigma a_{11}a_{22}}{P^2} + \frac{\Sigma (a_{11} + a_{22})g_{34}^2}{P^3} + \frac{(\Sigma g_{12}g_{34})^2}{P^4},$$

$$Z = \frac{\Sigma a_{11}a_{22}a_{33}}{P^3} + \frac{\Sigma a_{11}a_{22} \cdot g_{12}^2}{P^4}.$$

($\Sigma g_{12} \cdot g_{34}$ is written instead of $g_{12}g_{34} - g_{13}g_{24} + g_{14}g_{23}$.)

We have to consider two cases: 1° two of the coefficients a_{11} , a_{22} , a_{33} , and a_{44} are negative, and 2° the four coefficients are negative.

We may associate the equations (5) corresponding to different values of X , Y , and Z with the points of space. As no root of (5) may become zero or infinite, a change of the sign of the roots occurs only by passing twice the locus of the points, where (5) has equal roots. This locus or discriminantal surface is the developable ruled surface which is enveloped by the variable plane (5).

A discriminantal surface for the biquadratic equation has been introduced by Kronecker*; however, his equation has not the form of (5): the number of parameters has

* *Monatsberichte der Berliner Akademie*, 14 February, 1878.

been reduced by him by expelling the term with u^3 ; the surface arising in this way is not applicable for the present investigation. A description of the discriminantal surface for the equation (5) is to be found elsewhere*, and the regions are indicated in which the surface divides space. There are six regions corresponding with the nature and the sign of the roots of (5): 4 imaginary roots, 2 positive 2 negative roots, 2 imaginary 2 positive roots, 2 imaginary 2 negative roots, 4 positive roots, 4 negative roots.

The image-point Q_{irr} . for the irrotational equilibrium is lying either in the region of 4 positive roots or in the region of 2 positive and 2 negative roots. We have to inquire whether in both cases it is possible to displace the image-point into the region of stability, viz. the region of 4 negative roots.

For this aim we have to investigate the displacements :

$$\begin{aligned} X - X_0 &= \frac{\sum g_{12}^2}{P^2}, \\ Y - Y_0 &= \frac{\sum (a_{11} + a_{22})g_{34}^2}{P^3} + \frac{(\sum g_{12}g_{34})^2}{P^4}, \\ Z - Z_0 &= \frac{\sum a_{11}a_{22}g_{12}^2}{P^4}, \end{aligned}$$

which may be executed with the help of the gyroscopic forces. We see at once that the question is much more intricate than for the case of three degrees of freedom, because the expressions for the displacement of the image-point are no longer homogeneous with respect to the coefficients g . For small values of the g we first can neglect the term which disturbs the homogeneity, and we may find that the points we are able to reach lie inside a three-sided pyramid. For large values of the g , the neglected term becomes predominant when the inequality is fulfilled,

$$\sum g_{12}g_{34} \neq 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

These considerations, in connexion with an inspection of the discriminantal surface, will show that stabilization may always be obtained by sufficient values of the g , provided (6) be obeyed, for two and four instabilities.

* Christiaan Huygens, 1925.

CXIX. *The Mass-Spectra of Chemical Elements.*—Part VI.
Accelerated Anode Rays Continued. By F. W. ASTON,
Sc.D., F.R.S., Fellow of Trinity College, Cambridge.*

IN Part V. of this series of communications † the method of accelerated anode rays was described by which the mass-rays of a large number of metallic elements were produced in a form suitable for analysis by the mass-spectrograph. The present paper contains the results of further investigations by the same method during the year 1924. Although the anode ray discharge tube had to be repeatedly rebuilt during this period for purposes of cleaning and replacement its general design has not been altered substantially from that already illustrated ‡. The only change in detail worthy of note consists of setting back the surface of the composite anode several millimetres from the mouth of the pyrex tube containing it. This appears to result in a thinner but more concentrated beam of rays, but can only be advantageously applied in the fortunate circumstance of the beam being truly axially directed down the slit system of the spectrograph. As before, the extension of the method to new, and generally heavier, elements becomes increasingly difficult and the advances recorded here are nearly all dependent on the use of highly sensitive plates made by a schumannizing process recently described §. The successes obtained by incorporating the elements themselves into the anode, in the cases of tellurium and bismuth were to some extent unexpected and are probably due to the particular range of boiling points exhibited by these elements.

During the experiments on lead which only gave inconclusive results it was realized that the useful limit of work with the mass-spectrograph in use had been reached and it has now been dismantled to make room for a new one. The latter has been designed to give higher resolution and, more particularly, greater accuracy of measurement. If successful it will be used rather for the more exact comparison of the masses of known lines, with a view to determining their divergencies from the whole number rule, than for the analysis of more elements. This paper is therefore the last of the series and for that reason a complete list of all non-radioactive isotopes so far discovered is included in it.

* Communicated by the Author.

† *Phil. Mag.* xlvii. p. 385.

‡ *Loc. cit.* p. 387.

§ F. W. Aston, *Proc. Camb. Phil. Soc.* xxii. p. 548 (1925).

Indium (At. Wt. 114.8).

Indium is chemically very similar to gallium. It was therefore expected to yield to the same treatment. The fluoride was prepared from a sample of the metal kindly supplied by Professor T. W. Richards of Harvard, by solution in hydrofluoric acid. This incorporated into the anode gave a mass-spectrum showing one line only at 115. The mass of this appeared integral when compared with the lines of iodine and caesium. No great accuracy is claimed for these measurements and the line is too faint to exclude the possible presence of another isotope. Until further evidence is available on this point, indium is best regarded as a simple element of mass number 115.

Further experiments with Strontium.

The very bright anode beam given by this element* puts it next to lithium in value as a component of anode mixtures used in testing the setting of the discharge tube. In consequence many mass-spectra of it have been obtained. The more recent of these, though they confirm the previous conclusion that this element consists almost entirely of atoms of mass number 88, explain to a large extent the low value of its chemical atomic weight. In the first place the best plates give evidence of an extremely faint isotope 86 which appears to be present to the extent of about 3 or 4 per cent. In the second place the most accurate determinations of the mass of its principal constituent suggest that it is decidedly less than a whole number. For this purpose the lines of iodine and bromine were employed for reference. The chemical atomic weights of these elements (79.916 and 126.932) are used as substandards and have been determined with exceptional accuracy. The results of the mass-spectrograph indicate that we may confidently regard iodine as a simple element so that its line is taken as representing a mass of 126.93. The doublet of bromine has been recorded in all degrees of intensity on a large number of plates and, although the eye is particularly critical in judging the relative intensities of two similar images close together, no difference in intensity between the two components has been observed. It follows that its heavier isotope can be taken as of mass 80.92 with an accuracy at least exceeding one part in one thousand. Accepting these two values the strontium line gives the

* *Loc. cit.* p. 395.

same mean figure 87.8 for each comparison. The presence of Sr^{86} will bring this down a further fraction so that the discrepancy between the mean atomic weight calculated from the mass spectra and that accepted from chemical work 87.65 is no longer very serious.

Barium (At. Wt. 137.37).

The first successful experiments with barium were performed with anodes containing iodides and although they showed clearly that the mass number of its principal isotope was 138 the penumbra of the enormously strong and over-exposed iodine line prevented a critical search for lighter isotopes which its chemical atomic weight suggests. Work with other elements was therefore continued with lithium bromide replacing the iodide previously used for testing. By cleaning operations and continuous running with anodes free from iodine, this element was gradually eliminated from the apparatus until its line became sufficiently weak to warrant a further investigation of barium. In these experiments the anode consisted of a mixture of barium chloride and lithium bromide. Schumannized plates were used and the line Ba^{138} was obtained of very great intensity. Examination of the mass spectra showed that no mass number less than 136 could possibly be present to an appreciable extent. Slight asymmetry of the strong line suggested the possible presence, in very minute proportion, of 136, and since resolution in the neighbourhood of so strong a line is impossible on the instrument used, 137 may also be present. But even if both are present they cannot be so to an extent adequate to explain the chemical atomic weight now in use which appears therefore to be too low. In mitigation of this discrepancy, but not sufficient to explain it entirely, the principal line of barium, like that of strontium, appears to show a slight defect from a whole number mass.

Lanthanum (At. Wt. 138.91).

This rare earth element was investigated by means of its bromide which was prepared from a very pure specimen of the oxalate. A mixture of this with lithium bromide worked smoothly as an anode, but the results were not very intense. With an exposure of half an hour, however, a single line at 139 was obtained of such a strength as to make it reasonably certain that lanthanum is a simple element of mass number 139, as its chemical atomic weight would lead us to expect.

The plate was not suited to measurements of high accuracy but comparison with the iodine line showed no deviation from the whole number rule greater than that suggested by its atomic weight.

Praseodymium (At. Wt. 140·92).

The first experiments with this element using its fluoride were unsuccessful. Later, under better experimental conditions, results were obtained from the bromide made from a commercial sample (Schuchardt) of the oxide. The appearance of a line at 139 in addition to the one expected at 141 indicated that this was contaminated with lanthanum. Owing to the kindness of Dr. Auer von Welsbach, to whom the author is deeply indebted for a valuable collection of samples of rare earth salts, a specimen of the sulphate of praseodymium of exceptional purity was available. This was transformed into the bromide by treatment with strontium bromide and gave a single line at 141. It is therefore reasonably certain that praseodymium is a simple element of mass number 141. The chemical atomic weight, like that of lanthanum, suggests a mass slightly less than a whole number.

Neodymium (At. Wt. 144·27).

Neodymium bromide was prepared from a commercial sample (Drossbach) of the oxalate which, as results showed, was free from any serious contamination by neighbouring rare earth elements. The first attempts only yielded an indistinct band suggesting that the element was complex. Later, under particularly good experimental conditions with highly sensitive schumannized plates more definite effects were obtained. These indicated that neodymium certainly contains mass numbers 142, 144, and 146 not differing much in relative proportion, and possibly in addition (145) in smaller quantity. The latter must be regarded as doubtful for the present.

Cerium (At. Wt. 140·25).

Results from cerium were obtained by the use of the bromide prepared from a highly purified sample of the oxalate. Its most important mass line is 140 and shows no measurable deviation from a whole number. On the best mass spectra obtained a second fainter component 142 could be seen. The intensity of this line was in fair accord with

the chemical atomic weight given above. Cerium may therefore be taken as a complex element with mass numbers 140 and 142. The latter is isobaric with the lighter component of its neighbouring element neodymium.

Zirconium (At. Wt. 91?).

A very large number of abortive attempts have been made to obtain the mass spectrum of this element. Some of these have been mentioned in previous papers in this series. One of the points of special interest in connexion with zirconium is the uncertainty of its atomic weight owing to the discovery of hafnium. The integer 91 has been adopted by the International Committee pending accurate determinations by chemical methods, work on which is still in progress. Success with the mass spectrograph was only obtained by the fortunate combination of an exceptionally favourable setting of the anode ray generator and a remarkably sensitive plate. The anode contained a mixture of zirconium fluoride and lithium fluoride, but a considerable quantity of bromine was left in the apparatus from previous experiments. Three of the lines appearing, 90, 92, 94, can be ascribed with confidence to zirconium. A fourth faint one at (96) is doubtful, but may be another isotope. As regards the relative intensities of the lines there is little to rely on, a very rough estimate is 10, 2, 4, (1), respectively. The masses corresponding to the first three can be determined with unusually high accuracy owing to the incidental appearance among them of a faint doublet 91, 93 due to CBr. There is no indication of any asymmetry in the spacing of the five lines 90-94 so that the masses of the isotopes of zirconium must be very closely integral with those of bromine. This by the argument already used on p. 1192 makes them less than whole numbers by about one tenth of a unit. Putting in these values and the relative intensities estimated above, we get for the mean atomic weight 91.2 or 91.4 according as we exclude or admit the presence of the doubtful (96), but little reliance is to be put on these figures.

Cadmium (At. Wt. 112.41).

This element, unsuccessfully attacked before, has now yielded to improved experimental conditions. Using an anode containing a mixture of cadmium fluoride and lithium fluoride prolonged exposure yielded a mass-spectrum showing satisfactory intensity and detail. This was fortunate, for

cadmium is so complex an element and its lines so near the limit of resolution that without the enhanced resolving power given by the peculiar properties of the schumannized plates* it is doubtful if any reliable interpretation could have been made. Cadmium has six isotopes 110 (*c*), 111 (*e*), 112 (*b*), 113 (*d*), 114 (*a*), 116 (*f*). The relative intensities of the lines are indicated by the letters in alphabetical order, and agree reasonably well with the chemical atomic weight. The plates were not favourable for accurate determination of masses but these appear to be integral with that of iodine. It will be seen that the heaviest isotope is isobaric with the lightest isotope of tin the next higher element of even atomic number, but the most remarkable phenomenon observed is the extraordinary similarity between the groups of lines given by these two elements. If we except the still doubtful (Sn^{121}) and the heaviest isotope Sn^{124} , which does not appear to have its counterpart in the cadmium group, the intensity relations between the isotopes appear almost identical. The difference in mass number is 6, and if we place the lightest isotope at zero on the scale of mass number, each group will be found to consist of three strong even numbers 4, 2, 0 in descending order of intensity; then two nearly equal odd numbers 3, 1, and finally a fainter even number 6. This sequence of intensity relations is imitated, but less exactly, by selenium and krypton, and, quite possibly, by mercury. Such exact similarity as that exhibited by cadmium and tin is very significant and suggests that once the inner core of the nucleus, supposed the same for isotopes of the same element †, is formed the stability of nuclei produced by further additions to this core will be controlled by considerations which may be the same for cadmium as for tin.

Tellurium (At. Wt. 127.5).

Previous attempts to analyse this element by the use of its ethyl compound ‡, and by volatilizing the chloride and the element itself § had failed. Also during all the earlier work on accelerated anode rays any chance of success was improbable owing to the overwhelming strength of the iodine line the masking effect of which has already been referred to under barium. By the time the experiments on

* *Loc. cit.* p. 553.

† F. W. Aston, 'Nature,' 113, p. 395 (1924).

‡ *Phil. Mag.* xlii, p. 140 (1921).

§ *Phil. Mag.* xlv, p. 942 (1923).

cadmium were complete iodine had been rigorously excluded from the apparatus for a long time, and although its line could still be seen and used for reference its intensity was sufficiently reduced to warrant a further attack on tellurium. A fragment of pure redistilled tellurium was pulverized and incorporated into the anode paste used in the experiments on cadmium. The lines of tellurium were at once obtained and the result was repeated and confirmed with an anode of tellurium, lithium fluoride, and graphite only. The effects were not strong but sufficient for identification and measurement. Tellurium gives three lines of even mass number 126, 128, 130. The intensities of the two latter appear about equal and double that of the first. The iodine line was too faint to be distinguished on these plates but comparative measurements could be made against the lines of bromine. These indicate that the masses may be a little less than whole numbers but there is no reason to suppose that the defect is abnormally great. Hence from the intensities of the lines it seems probable that the mean atomic weight is at least as high as 128. Owing to its anomalous position with regard to that of iodine (of which these results supply the obvious explanation) the atomic weight of tellurium has received an exceptional amount of attention from chemists and all their later determinations give a value considerably less than this. The discrepancy is of about the same order as that noted in the case of barium, but of the opposite sign. No explanation can be suggested in either case at present.

Tellurium is unique among the elements so far analysed as it seems probable that *all* its mass numbers form members of isobaric pairs. They are shared by xenon, the element of next higher even atomic number.

Bismuth (At. Wt. 209.00).

The boiling point of bismuth is not much higher than that of tellurium so that there was some reasonable hope that it would yield to corresponding treatment. Metallic bismuth was ground into the anode paste and after a long exposure with the anode worked at a white heat it gave a single line in the position expected from its atomic weight. This line was very faint, and owing to the great mass lay in a part of the plate unfavourable for measurement, but comparisons with the lines of mercury leave little reason to doubt that bismuth is a simple element of mass number 209. Its atom is therefore the heaviest weighed on the mass spectrograph.

Further experiments on Silicon, Iron, and Lead.

Silicon.—In the first analysis of silicon * some evidence was adduced for the existence of an isotope Si^{30} but owing to the possibility of hydrides this could not be regarded as conclusive at the time. Later valuable support was obtained in the study of the band spectra of silicon compounds by Mulliken†. During one of the experiments on zirconium fluoride described in this paper the mass lines of silicon were obtained under conditions which precluded the presence of hydrides. In addition to the very strong line Si^{28} its two fainter companions Si^{29} and Si^{30} were clearly shown, the latter being rather less intense than the former in excellent agreement with the conclusions of Mulliken. Silicon may therefore be accepted as consisting of three isotopes. It is difficult to estimate the relative proportions accurately but the evidence of the mass-spectrograph is generally in favour of a mean atomic weight slightly higher than the one 28.06, recently adopted by the International Committee. The earlier value was 28.3.

Iron.—During some tests of a setting of the anode ray tube for efficiency, an anode containing bromide of iron was employed in the hope of obtaining the principal line Fe^{56} so strong that the question of the presence of the doubtful faint component Fe^{54} could be settled. Under such conditions the presence of a line at 54 could not be ascribed to adventitious organic or other molecules. On one occasion an exceptionally strong beam of rays was obtained and both lines appeared in an entirely satisfactory manner. The ratio of the line 54 to the predominant 56 could be roughly estimated at about 1 to 20. The most probable value of the mass of the latter has been given‡ as 55.94. The presence of 5 per cent. of an isotope two units lighter will shift the atomic weight back by one tenth of a unit so that the results of the mass-spectrograph are in good agreement with the accepted atomic weight of 55.84.

Lead.—This element, which is of peculiar interest owing to our knowledge of its isotopes formed in radioactive disintegrations, has a boiling point not very much higher than that of bismuth and so might be expected to yield, though less easily, to the same treatment. Finely divided metallic lead scraped from a reduced negative accumulator plate incorporated into the anode mixture has given faint but positive

* Phil. Mag. xl. p. 630 (1920).

† R. S. Mulliken, 'Nature,' 113, pp. 423, 489 (1924).

‡ Phil. Mag. xlv. p. 941 (1923).

Table of Elements and Isotopes *.

| Element. | Atomic number. | Atomic weight. | Minimum number of isotopes. | Mass-numbers of isotopes in order of intensity. |
|----------|----------------|----------------|-----------------------------|-------------------------------------------------|
| H | 1 | 1.008 | 1 | 1 |
| He..... | 2 | 4.00 | 1 | 4 |
| Li..... | 3 | 6.94 | 2 | 7, 6 |
| Be..... | 4 | 9.02 | 1 | 9 |
| B..... | 5 | 10.82 | 2 | 11, 10 |
| C..... | 6 | 12.00 | 1 | 12 |
| N..... | 7 | 14.01 | 1 | 14 |
| O..... | 8 | 16.00 | 1 | 16 |
| F..... | 9 | 19.00 | 1 | 19 |
| Ne..... | 10 | 20.20 | 2 | 20, 22 |
| Na..... | 11 | 23.00 | 1 | 23 |
| Mg..... | 12 | 24.32 | 3 | 24, 25, 26 |
| Al..... | 13 | 26.96 | 1 | 27 |
| Si..... | 14 | 28.06 | 3 | 28, 29, 30 |
| P..... | 15 | 31.02 | 1 | 31 |
| S..... | 16 | 32.06 | 1 | 32 |
| Cl..... | 17 | 35.46 | 2 | 35, 37 |
| A..... | 18 | 39.88 | 2 | 40, 36 |
| K..... | 19 | 39.10 | 2 | 39, 41 |
| Ca..... | 20 | 40.07 | 2 | 40, 44 |
| Sc..... | 21 | 45.1 | 1 | 45 |
| Ti..... | 22 | 48.1 | 1 | 48 |
| V..... | 23 | 51.0 | 1 | 51 |
| Cr..... | 24 | 52.0 | 1 | 52 |
| Mn..... | 25 | 54.93 | 1 | 55 |
| Fe..... | 26 | 55.84 | 2 | 56, 54 |
| Co..... | 27 | 58.97 | 1 | 59 |
| Ni..... | 28 | 58.68 | 2 | 58, 60 |
| Cu..... | 29 | 63.57 | 2 | 63, 65 |
| Zn..... | 30 | 65.38 | 4 | 64, 66, 68, 70 |
| Ga..... | 31 | 69.72 | 2 | 69, 71 |
| Ge..... | 32 | 72.38 | 3 | 74, 72, 70 |
| As..... | 33 | 74.96 | 1 | 75 |
| Se..... | 34 | 79.2 | 6 | 80, 78, 76, 82, 77, 74 |
| Br..... | 35 | 79.92 | 2 | 79, 81 |
| Kr..... | 36 | 82.92 | 6 | 84, 86, 82, 83, 80, 78 |
| Rb..... | 37 | 85.44 | 2 | 85, 87 |
| Sr..... | 38 | 87.63 | 2 | 88, 86 |
| Y..... | 39 | 88.9 | 1 | 89 |
| Zr..... | 40 | (91) | 3 (4) | 90, 94, 92, (96) |
| Ag..... | 47 | 107.88 | 2 | 107, 109 |
| Cd..... | 48 | 112.41 | 6 | 114, 112, 110, 113, 111, 116 |
| In..... | 49 | 114.8 | 1 | 115 |
| Sn..... | 50 | 118.70 | 7 (8) | 120, 118, 166, 124, 119, 117, 122, (121) |
| Sb..... | 51 | 121.77 | 2 | 121, 123 |
| Te..... | 52 | 127.5 | 3 | 128, 130, 126 |
| I..... | 53 | 126.92 | 1 | 127 |
| X..... | 54 | 130.2 | 7 (9) | 129, 132, 131, 134, 136, 128, 130, (126), (124) |
| Cs..... | 55 | 132.81 | 1 | 133 |
| Ba..... | 56 | 137.37 | (1) | 138 |
| La..... | 57 | 138.91 | 1 | 139 |
| Ce..... | 58 | 140.25 | 2 | 140, 142 |
| Pr..... | 59 | 140.92 | 1 | 141 |
| Nd..... | 60 | 144.27 | 3 (4) | 142, 144, 146, (145) |
| Hg..... | 80 | 200.6 | (6) | (197), 202, 204, 198, 199, 200 |
| Bi..... | 83 | 209.00 | 1 | 209 |

* Including Dempster's results.

results. These indicate that common lead is a complex element, as was to be expected, but since there is little hope of obtaining definite information on its constitution with the apparatus used it has been decided to defer further investigation until a mass-spectrograph of higher resolving power is available.

Survey of Elements yet to be analysed.

It will be seen from the table that of the 80 non-radioactive elements known to exist, 56 have yielded fairly definite analyses. The experience gained during the work enables the probabilities of further progress to be estimated as follows :—

Niobium, molybdenum, rhodium, ruthenium, and palladium present great difficulties. All seem very unsuitable to the method of anode rays on account of their chemical properties. The first two might be attacked by the ordinary method by means of their volatile fluorides. Exactly the same reasoning applies to the corresponding elements tantalum, tungsten, osmium, iridium, and platinum but still greater difficulty is to be expected owing to their higher atomic weights. Elements 62–71 of the rare earths are all quite hopeful, faint effects have already been obtained from erbium (68), but a mass-spectrograph more suitable to rays of high mass number is desirable for their satisfactory analysis, just as for lead. Hafnium should be amenable to the form of treatment which succeeded with zirconium but some method of increasing the strength of the rays will have to be devised to overcome the adverse effect of greater mass, to which past failures are ascribed. A serious obstacle to the analysis of gold and thallium, which belong to groups reasonably favourable to anode ray production, is the purely technical one of eliminating mercury completely. Further difficulties in the case of gold are its inability to form compounds stable at high temperatures and its very high boiling point.

With regard to those elements only known in radioactive forms the majority cannot be directly investigated owing to the impossibility of obtaining sufficient material. Of the emanations, which being inert gases are particularly favourable to treatment in the discharge tube, radon only could be obtained in suitable quantity. The indirect evidence obtained from the study of radioactivity leaves very little doubt that it is simple of mass number 222 so that considering the disastrous after effects of the substance on the apparatus it is questionable if the experiment is worth while. Much the same arguments apply to radium itself which could be

attacked on the same lines as barium, though probably with greater difficulty.

The parent elements thorium and uranium appear most hopeless of all for each is the heaviest member of a chemical group already found highly unfavourable to mass spectrum analysis. This is unfortunate for chemical evidence suggests that both are complex and a direct identification of their more important isotopes might be of the greatest value in explaining difficulties connected with the radioactive disintegration series.

In concluding this series of papers the author wishes again to express his cordial thanks to all who so kindly supplied materials for the analyses and to the Government Grant Committee of the Royal Society for some of the apparatus employed.

Summary.

Further investigations by the method of accelerated anode rays are described by which the constitutions of ten more elements Indium, Barium, Lanthanum, Praseodymium, Neodymium, Cerium, Zirconium, Cadmium, Tellurium, and Bismuth have been determined.

Evidence is given for an additional isotope of Strontium and isotopes of Silicon and Iron previously doubtful have been satisfactorily confirmed.

Some results have been obtained from lead but are not considered conclusive.

A general survey of the remaining elements is made and the possibility of their analysis discussed.

A complete list of all isotopes so far determined is given.

Cavendish Laboratory, Cambridge.

February, 1925.

CXX. *On the use of Monochromatic X-Rays in the production of Laue Diagrams, and on the Structure of Mother-of-Pearl.*
By J. H. SHAXBY, D.Sc., F.Inst.P.*

[Plate XIII.]

THE usual pattern of Laue spots, produced by a high-tension source generating a continuous X-ray spectrum, presents certain difficulties of interpretation, as the position of a given spot depends on two unknown quantities, the architecture of the crystal and the wave-length of the ray

* Communicated by the Author.

forming the spot. If, on the other hand, monochromatic X-rays are employed, of known wave-length, the number of spots is so much reduced that in many cases little information can be drawn from the pattern as to the crystal structure. In some cases, however, the number of spots is sufficient and interpretation then becomes simple, because the wave-length is definite and known. If the tension across the tube is not too great, and if the crystal is thin or its atoms are of comparatively low atomic number, its transparency to the K-rays of the anticathode renders the effective wave-length that of the K doublet; the continuous spectrum plays a negligible part. If, on the other hand, the crystal is strongly absorptive or a subsidiary filter is introduced, the K rays become quite subordinate to the filtered residue of the continuous spectrum. The transmitted beam in this case is still approximately monochromatic and is of wave-length a little longer than the quantum limit corresponding to the tension employed. Its effective value can be determined spectrographically or by calculation from the known absorption coefficients of the crystal (or subsidiary filter). This wave-length is now independent of the material of the anticathode, for instance, in the experiments described below the pattern obtained was the same with anticathodes of silver and of tantalum, under the same tension, 40 kilovolts.

I have carried out experiments of this nature in determining the structure of mother-of-pearl (nacre), using the apparatus excited at constant tension described by Dr. A. Dauvillier *, consisting of a motor-generator supplying alternating current of 600 cycles per second, used in connexion with a high tension transformer and pairs of condensers and kenotrons. The apparatus thus provides current which, at a tension of 40 kilovolts, is constant to within 1 per cent.

The tube is of quartz and is about 2 inches in diameter; the anticathode, fitted with a screwed-in and readily changed target, is water-cooled, and the thin celluloid window is likewise cooled by an air blast. The cathode hot wire of tungsten is supplied with 3.0 to 3.75 amperes, and the cathode is earthed through a high-frequency choke. The tube when in operation was connected to a glass condensation pump, backed by a Gaede pump, the initial vacuum being obtained by a rotary oil-pump.

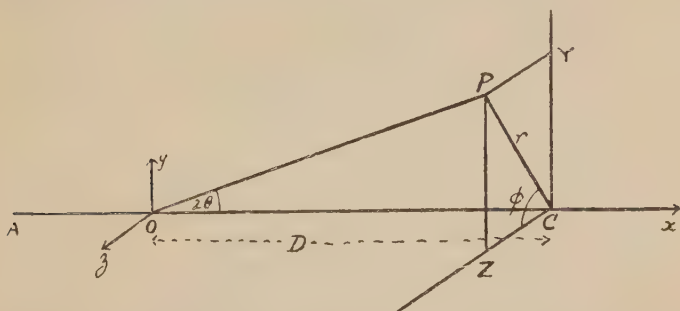
In most of the experiments with mother-of-pearl the tube was fitted with a silver target and was run at a tension of 40

* *Jour. de Physique*, iii. p. 154 (1922).

kilovolts ; with about 20 milliamperes an exposure of 4 hours was sufficient for specimens 1 cm. thick.

In investigating a method of differentiating natural pearls (perles accidentelles) from the Japanese artificial pearls (perles de culture Japonaise), Dauvillier* found that mother-of-pearl gave diffuse Laue spots. With certain orientations of the specimen (incident beam normal to the laminations of the substance) 6 spots appear in a more or less regular hexagonal pattern, while with others (beam parallel to laminations) a considerable number of spots appear, approximately in a rectangular formation.

To improve the definition of the spots as far as possible in the present series of measurements, a tubular collimator was mounted inside the X-ray bulb† and a lead block pierced with a small hole was mounted a few centimetres in front of the window. The specimens were affixed to this block over the aperture and the narrow pencil of rays thus defined produced the Laue pattern upon a photographic plate set up about 11 cm. beyond the nacre. The spots were sufficiently sharp to permit their distances from the central spot to be measured with an accuracy of about 2 per cent.



(2) Let AO be the narrow incident pencil of X-rays falling upon a diffracting crystal placed at O, the origin of coordinates. Let C be the position of the central undiffracted spot, P that of a Laue spot. Let $OC = D$, and let θ be the grazing angle for the set of atomic planes which give rise to the spot P, so that the angle $COP = 2\theta$. Let angle $PCZ = \phi$.

Then, if l, m, n , are the direction cosines of the normal to the planes of atoms considered, it is clear that

$$l = -\sin \theta ; m = \cos \theta \sin \phi : n = \cos \theta \cos \phi.$$

* C. R. clxxix. p. 819 (1924) ; *Jour. de Physique*, p. 123 (1924).

† The tube is essentially that figured at p. 85 of 'La Technique des Rayons X' : Dauvillier (*Conf. Rapp. sur la Physique*, Paris, 1925).

If we call l', m', n' the direction cosines of the normal to the planes producing a second spot, and ψ the angle between the two normals,

$$\begin{aligned}\cos \psi &= ll' + mm' + nn' = \sin \theta \sin \theta' \\ &\quad + \cos \theta \cos \theta' (\sin \phi \sin \phi' + \cos \phi \cos \phi') \\ &= \cos \theta \cos \theta' \cos (\phi - \phi') + \sin \theta \sin \theta'.\end{aligned}$$

Hence if the Laue spots are near C , so that θ and θ' are small, $\psi = (\phi - \phi')$, or the angle between the radii drawn from C to the two spots is equal to the angle between the two sets of planes responsible for the two spots.

Also the distance d between consecutive atomic planes giving rise to a Laue spot is equal to $\lambda/2 \sin \theta$ (θ being known from the equation $r = D \tan 2\theta$, where r is the distance of the spot from C), and d is practically the distance between the neighbouring principal planes perpendicular to plane yz in the direction specified by ϕ . Thus the distribution of atoms in the yz plane is known.

Plate XIII. shows the general form of the Laue pattern when the incident X-rays are parallel to the laminations of the specimen of mother-of-pearl. In the case shown the plane perpendicular to the rays is the (100) plane, the diagram when they are normal to the (010) plane is essentially similar, with altered values of ϕ and r . When the rays are incident normally to the laminations the symmetry is sixfold, and the spots are very diffuse*.

3. Chemical analyses of nacre † show that it consists of calcium carbonate (75 per cent. to 90 per cent.), organic material, chiefly conchyolin, and water. The relative proportions of the two latter constituents are very variously stated. This composition is thus very similar to that of true pearl, which contains about 92 per cent. of calcium carbonate and 4 per cent. or 5 per cent. of conchyolin ‡. The organic matter appears to form a meshed or honeycomb structure, in the cells of which the mineral substance is deposited as minute crystals, by migratory calciferous cells §. In the pearl the conchyolin alveoli form a radial framework, so the pearl is built up of concentric shells, like the coats of an onion.

The cells in which the calcium carbonate is deposited are of optical dimensions, of the order of 1μ , and this structure

* *C. R.* clxxix. p. 1602 (1924).

† L. Boutan, *Bull. de la Station biol. d'Arcachon* (1921).

‡ G. & H. Harley, *Proc. R. S.* xxiii. p. 461 (1888).

§ R. Dubois, *C. R.* cxxxviii. p. 710 (1904).

is responsible for the lustre and iridescence of pearls and nacre.

The calcium carbonate is in the form of aragonite. The atomic structure of this mineral has been the subject of an *a priori* study by Huggins*, and radiometric measurement by W. L. Bragg†. Aragonite crystallizes in the orthorhombic system and possesses a quasi-hexagonal symmetry about the *c*-axis. The three axes are in the ratios, $a : b : c = 0.623 : 1 : 0.720$ ‡.

Huggins concluded that $a = 3.930 \text{ \AA}$, $b = 6.310 \text{ \AA}$, and $c = 4.546 \text{ \AA}$, and that the unit of crystalline structure contains $2(\text{CaCO}_3)$. Bragg's experiments led him to ascribe aragonite to the holosymmetric class of the orthorhombic system, with a crystalline unit containing $4(\text{CaCO}_3)$. The three axes are of lengths 4.94 \AA , 7.94 \AA , and 5.72 \AA , and the arrangement of atoms is quite different from that supposed by Huggins.

4. The measurements I have made with mother-of-pearl entirely confirm Bragg's model. It will suffice to quote the results of the measurements of plates furnished by rays parallel to the laminations of the nacre and approximately in the (100) and in the (010) directions. (Tables I and II.)

TABLE I.
Effective wave-length 0.40 \AA .

| Observed ϕ° . | Calculated. | Observed $d(\text{\AA})$. | Calculated. |
|-------------------------|-------------|----------------------------|-------------|
| 0 | 0 | 2.42 | 2.49 |
| 22.5 | 23.4 | 2.26 | 2.265 |
| 38 | 40.9 | 3.53 | 3.385 |
| 57 | 60.0 | 2.41 | 2.47 |
| 68 | 68.9 | 1.76 | 1.77 |
| 90 | 90 | 2.90 | 2.86 |

TABLE II.

| Observed ϕ° . | Calculated. | Observed $d(\text{\AA})$. | Calculated. |
|-------------------------|-------------|----------------------------|-------------|
| 0 | 0 | 3.89 | 3.97 |
| 36 | 34.8 | 2.84 | 2.92 |
| 54.5 | 54.3 | 4.04 | 4.11 |
| 70 | 70.2 | 2.41 | 2.36 |

Bragg gives an interesting description and diagram of the

* Phys. Rev. xix. p. 354 (1922).

† Proc. R. S., A. cv. p. 16 (1924).

‡ Groth, *Chem. Krystallographie*, ii. p. 200.

common mode of twinning, across the 110 planes. It will be seen that this twinning and the fact that the symmetry about the *c*-axis is pseudo-hexagonal and not perfect—the angles are $58^{\circ} 8'$ and $60^{\circ} 56'$ —lead to a changing orientation of those faces which are parallel to the *c*-axis. This produces a sufficient variation in the angle of incidence of the X-rays upon the planes rich in atoms to permit a narrow range of wave-lengths to produce a considerable number of spots. The correct incidence is attained much as in the case of rotating crystals. The quasi-hexagonal *c*-axis retains its direction, hence the effect is not like that of a heterogeneous crystalline powder: the heterogeneity is partial and is further only two-dimensional. With photographs taken by means of rays travelling in the direction of the *c*-axis this change of orientation makes itself felt in the greater diffuseness of the spots and in some cases in their almost complete fusion into a ring, somewhat resembling a solar halo with six mock-suns.

Mother-of-pearl thus consists, so far as its mineral constituents are concerned, of aragonite crystals whose quasi-hexagonal axes are perpendicular to the planes of lamination.

I wish to express my sincere thanks to M. le Duc de Broglie, in whose laboratory the work was carried out, and to Dr. A. Dauvillier, for much advice and assistance.

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Cardiff.

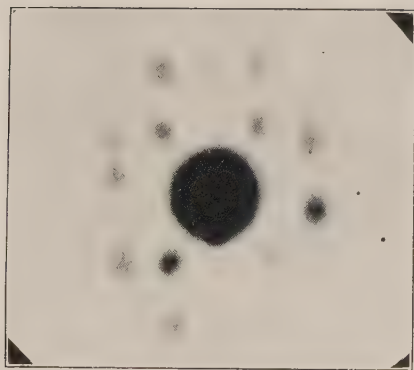
CXXI. *Emission Band Spectra of Aromatic Compounds.*
Part II.—*Their Origin.* By JOSEPH KENNETH MARSH,
*D.Sc.**

IN the previous paper † it has been shown that in every case which has come under notice of multiple banding in emission spectra there is evident a difference between the successive frequencies amounting to the absolute frequency of a band in the near infra-red absorption spectrum. It therefore seems obvious that the physical significance of the bands in both instances will be similar, and as in the case of the infra-red bands a fairly complete and satisfactory explanation has been arrived at, the way seems open for an extension of the same principles to the regions of higher frequency.

Briefly it may be stated that these infra-red bands are supposed to be due to the quantized vibration of groups of

* Communicated by the Author.

† *Suprà*, p. 971.



atoms, or molecules. If a disturbance is taking place in a molecule it follows that the forces existing between the atoms are in a state of change. In the case of a diatomic molecule the equilibrium existing between the electrostatic and gravitational forces is disturbed and there results a vibration of the atoms in their line of junction. Absorption bands of the quantum frequency of this vibration are seen in the near infra-red. These, however, are not simple bands but under high dispersion are capable of resolution into series of finer bands at approximately equal intervals, these bands being due to the changes in the rotational energy of the molecule. Further, the pure rotation spectrum may be observed in the far infra-red ($\lambda > 100\mu$). If ν_v is a vibration frequency and ν_r a rotation frequency, in the near infra-red spectrum bands expressible by the formula $\nu_v \pm \nu_r$ will be found. Such bands are known as rotation-vibration bands. The best examples are found in the case of the halogen acids which have been examined by Imes (Astrophysical J. l. p. 251 (1919)). Due to the changes in the moment of inertia during vibration and changes of centrifugal forces during rotation these two motions have mutual effects, which may be observed in the spectra. The rotation-vibration bands are caused to be bunched together towards the high frequency end instead of being evenly distributed, whilst the overtone vibration bands become shifted to positions rather less than exact whole number multiples of their fundamentals.

Due to the movements of the electrons in their orbits we obtain in the ultra-violet or visible regions absorption or fluorescence spectra of organic compounds. If the frequency due to the electronic jump is ν_e and the molecule is simultaneously emitting or absorbing vibrational and rotational energy at frequencies ν_v and ν_r we may find in the spectrum all the frequencies $\nu_e \pm m\nu_v \pm n\nu_r$ where m and n are small whole numbers. Further, in a complex molecule there may be more than one type of vibrational motion between the atoms, *i.e.*, there may be more than one term represented by $m\nu_v$.

If the electronic energy is undergoing an increase ν_e should be observed as an absorption band; if a decrease, as an emission band. From the experimental fact that as a general rule absorption and emission do not overlap extensively in the case of organic compounds, but are contiguous, the emission being of lower frequency than the absorption, we may infer that both emission and absorption cannot occur at $\nu_e + m\nu_v$ but only the former, and at $\nu_e - m\nu_v$ only

the latter. On this basis the electronic frequency may be said to occur at the boundary between the emission and absorption regions. Further, we may infer that whilst electronic energy is both absorbed and emitted we only have evidence of the absorption of atomic vibrational energy. This is true also in the infra-red, banded emission spectra never having been observed.

We may now turn to a consideration of some individual spectra.

The Spectra of Benzene.

The absorption bands of benzene have been measured with the greatest accuracy by Henri (J. Phys. Rad. iii. 181 (1922)), who found that they could be represented by a formula derived from a consideration of the energy contents of the molecule. In two states the electronic, atomic, and molecular energy will be represented by

$$W_e + W_a + W_m = Bh + phb + \frac{h^2 q^2}{8\pi^2 I} \quad . \quad . \quad (1)$$

$$W_e + W_a + W_m = Ah + nha + \frac{h^2 m^2}{8\pi^2 I} \quad . \quad . \quad (2)$$

The formula representing the observed band systems is

$$\nu = A - B + na - (pb + p^2 b') + \alpha(m^2 - q^2), \quad . \quad . \quad (3)$$

which is derivable from 1 and 2 with the exception of the term $p^2 b'$, the value of which, however, is very small. The high frequency term $A - B$ in 3 which determines the general region of absorption is electronic in origin. The large band systems such as persist in solution as well as the finer band systems (terms in a and b in 3) are atomic, whilst the finest structure is molecular.

A formula similar to that deduced by Henri is found to fit the fluorescence bands. He divided all the bands observed into four series having different values for the term $A - B$ in 3. Three of these series had $a = 921.4$, $b = 152$, $b' = 2$, but the fourth had $b = 166$, $b' = 0$. The electronic and atomic terms of the second of these series are given by the formula

$$\nu = 37494 + 921.4 n - (159p + 2p^2).$$

(*Note.*—these figures represent waves/cms., whereas in the previous paper we have used a unit ten times this size *i.e.*, waves/mm.) This may be written

$$\nu = 37494 + 6n159(1 - .0358) - 159.2p(1 + .01257p) \quad . \quad . \quad (4)$$

All the chief bands in the fluorescence spectrum are well

represented by the formula

$$\nu = 37494 - 6n159(1 + \cdot 0358) - 159 \cdot 2p(1 + \cdot 01257p), \quad (5)$$

which differs only from the absorption formula in the matter of signs. In the table below the calculated positions of the chief bands, according to the above formula, are confronted with the observed frequencies.

| Calc. | Obs. | Calc. | Obs. | Calc. | Obs. |
|--------|-----------|--------|-------|--------|--------|
| $n=0.$ | | $n=1.$ | | $n=2.$ | |
| 37494 | 37490 | 36504 | 36510 | 35514 | 35520 |
| 37335 | 37340 | 36345 | 36350 | 35355 | 35360 |
| 37174 | 37170 | 36184 | 36180 | 35194 | 35200 |
| 37007 | 37000 | 36017 | — | 35027 | 35040 |
| 36830 | 36830 | 35840 | 35860 | 34850 | 34870? |
| 36639 | 36630 | 35749 | 35750 | | |
| $n=3.$ | | $n=4.$ | | $n=5.$ | |
| 34524 | 34530 | 33534 | 33540 | 32544 | 32540 |
| 34365 | 34360 | 33375 | 33370 | 32385 | 32370 |
| 34204 | — | 33214 | — | 32224 | 32220 |
| 34037 | 34050 | 33047 | — | 32057 | 32040 |
| 34860 | 34890-770 | 32880 | 32880 | | |

The correcting factors $\cdot 01257p$ in the last term of 4 and 5 corresponds to what is found to be required for the expression of the successive overtone bands of a rotation-vibration spectrum to make allowance for the effect of the rotation on the vibration. This points to the benzene bands being successive overtones of a band of frequency 159, and to their having the same physical significance as rotation-vibration spectra.

The features of the benzene spectrum which it is desirable to explain are (1) the recurrence of bands at intervals of 159 units; (2) the recurrence of bands at intervals of 921·4 or 987 units; (3) the cause of the difference of this interval in the case of absorption and emission; (4) the cause of the difference of the most refrangible band from the others, and of the double or triple heads observed in the other bands.

The Kekulé formula for benzene represents it as a condensation of three molecules of ethylene, and as the infra-red spectrum will have to be considered parallel with the ultra-violet, we shall start by examining the infra-red spectrum of ethylene. (See diagram in previous paper.) The four outstanding bands are:—

| No. | 1 | 2 | 3 | 4 | (5) |
|-----------------|------|------|------|-------|----------|
| λ | 3·28 | 5·3 | 6·98 | 10·5 | (21·0) |
| ν | 3049 | 1887 | 1433 | 952·4 | (476) |
| Diff. | — | 454 | 481 | 476 | 476 |

Nos. 2, 3, and 4 are obviously overtones of a band (No. 5) at about 21μ , ν 476 which is beyond the limit to

which measurements have been carried. No. 1 does not belong to the same series. Thus characteristic of ethylene are bands at intervals of 476 units, multiples of an hypothetical fundamental of this frequency. Now this value is just three times the interval 159 found for the absorption and emission bands of benzene. It appears then that the spectrum of benzene is derived from that of ethylene, but concurrently with the condensation of the three ethylene bands together a diminution of the ethylene frequency to $\frac{1}{3}$ of its normal value takes place. The frequency of the ethylene band No. 1 will likely be affected similarly, and we must therefore look for a strong benzene band at 3.28×3 , *i. e.*, 9.84μ . Actually the strongest band of benzene is found at 9.8μ . Thus we find ethylene has two characteristic frequencies 3049 and 476, and in benzene both these are reduced to $\frac{1}{3}$ the value, 1020 and 159. The question now arises as to what influence the frequency 1020 has on the absorption and emission spectra of benzene. Considering first the emission spectrum we have regarded the position $\nu = 37494$ as the zero point, *i. e.*, the electronic frequency. By subtracting from this successive multiples of 159 we get the series of bands forming the first (F) group (See Pl. X.*). At 36474 we might expect a band due to the frequency 1020 and at 37540 the sixth multiple of the 159 series. There might also be a third band mid-way between these two due to their cooperative effect. Actually all three are seen. A faint band corresponding to the 6th multiple of 159 occurs in front of the head of band E. The strong head is double, consisting of two components $37494 - \frac{(1020 + 954)}{2}$ and $37494 - 1020$. Subsequent bands of group E have frequencies approximately $159n$ less than one or other of these two bands. Taking the head of E as a new zero point we should have for the head of D frequencies $(1020 + 954)/2$ and 1020 less, but the head of Group E being itself double we obtain three strong bands in Group D for every one seen in F. Further, the multiples of 159 have successively less influence with the 2nd, 3rd, and 4th multiples of 1020, so that there is a gradual transition of the interval between the strongest bands to 1020 units, but meanwhile the spectrum becomes very indistinct. A subsidiary system of bands occurs at intervals of $159/2$. In the benzene emission spectrum we have usually taken the larger periodicity as 987, which is a mean between 954 and 1020, and the whole spectrum is explicable as a resultant of two vibrations 1020 and 159. In the absorption spectrum the periodicity is decreased below 954 by exactly the same

* Phil. Mag. May 1925,

amount as in emission it is increased above this figure, and periodicities of 921 and 159 are found (Henri, *loc. cit.*) ; 954 or 6×159 is therefore the mean of the absorption and fluorescence values.

The main features of the benzene spectra are explicable as resulting from the compounding of two infra-red frequencies. Of these the smaller appears to be characteristic of ethylenic compounds *i.e.*, of the $C=C$ linkage, but the larger differs but slightly from the ordinary value of a vibration common to all compounds with CH groups. Benzene and its derivatives have a band at about 3.25μ , whilst in aliphatic compounds it is found at about 3.43μ . To obtain the interval found in the benzene spectrum (1020) the frequency of this band (3077) must be divided by the factor 3. With other substances other factors may be required. Thus the intervals of about 400, 750–800, or 1600 units found in the aliphatic substituted type of spectrum may be regarded as eighths, quarters, or halves of the 3.25 region frequency. This band should therefore be at least the 24th multiple of a fundamental which will have a frequency of 128.25. Most of the infra-red absorption maxima considered by Coblentz as characteristic of benzene are found to be accurately expressed as multiples of such a frequency. This will be seen from columns 2 and 3 of the following table, though the correspondence of the higher multiples is less exact than of the lower, probably due to the accumulation of the small rotational effects previously mentioned. The band at 11.8μ is seen to have an independent origin. In the last column the positions of the bands which Coblentz considered characteristic of CH_2 or CH_3 groups are given for the purpose of comparison with the position of a parallel series in benzene. There can be little doubt that both these series have their origin in CH vibrations but that the frequency is somewhat raised in benzene and derivatives. The raising of the frequency means that there is more energy in the CH bond or that the H is bound tighter when the carbon atom to which it is attached has a large amount of unsatisfied valency. From the study of the infra-red absorption spectrum of acetylene made by Coblentz it can be seen that a triple bond has an even more pronounced effect. He found the corresponding band at 3.08μ in this case. The following examples demonstrate the effect admirably.

| | | |
|-----------|----------------|--------------|
| Acetylene | $HC \equiv CH$ | 3.08μ . |
| Ethylene | $H_2C=CH_2$ | 3.28μ . |
| Ethane | H_3C-CH_3 | 3.39μ . |

The value for higher aliphatic hydrocarbons further rises slightly to a constant value of 3.43 or 3.44μ with chains of five or six carbon atoms, suggesting that with the completion of an open ring a satisfaction of part of the residual affinity of carbon is attained. In the case of the isomeric xylenes it is found that when the CH_3 groups are far apart the benzene band at 13μ is not disturbed, but when they approach to the ortho position the band is found at 13.6μ , or nearly the normal position for aliphatic compounds.

| Characteristic Infra-Red bands of Benzene as multiples of ν 128.25. | | | Characteristic Aliphatic CH Bands. |
|----------------------------------------------------------------------------|--------------------|------------------|---------------------------------------|
| <i>Multiple.</i> | <i>Calculated.</i> | <i>Observed.</i> | |
| | ν | ν | ν |
| 6 | 13.0 | 12.95 11.8 | 13.6-13.8 |
| 8 | 9.75 | 9.78 | |
| 9 | 8.67 | 8.67 | |
| 12 | 6.50 | 6.75 | 6.86 |
| 24 | 3.25 | 3.25 | 3.43 |
| 32 | 2.44 | 2.49 | |
| 36 | 2.17 | 2.18 | |
| 48 | 1.63 | 1.68 | 1.71 |
| 96 | .813 | .84 | .86 |

From the point of view of the mechanism of the benzene molecule it is interesting, now that we have established the connexion of the benzene bands at intervals of 159 units with the vibration between carbon atoms, to note again that these bands show evidence that the atoms originating them are in a state of rotation with regard to one another. This must mean that the carbon atoms in the molecule circulate in orbits so that their distances from the centre of the molecule will vary. Carbon atoms 1 and 2 are at extreme phases of such orbits in the accompanying diagram (p. 1213).

The recent analysis of the band at 3.25μ in benzene by Meyer and Bronk (Phys. Rev. 1923, xxi. p. 712) into bands at $1/\lambda$ 3093.0, 3050.3 and 2965.4, showing intervals of 42.7 and 84.9, suggests that here we have direct evidence of the rotation of CH groups. The moment of inertia of a system giving an interval of 42.5, assuming it to have one quantum of rotational energy, will be 1.31×10^{-40} , which is very near the values found for HF or H_2O on the same assumption. The CH vibration in the case of the benzene molecule appears to be an integral multiple of the CH rotation frequency. Thus the rotation bands of Meyer and Bronk are at intervals almost exactly $\frac{1}{3}$ and $\frac{2}{3}$ the magnitude of the fundamental vibration 128.25, but for the characteristic CH bands six times this fundamental would be a small enough basic unit, and the rotation frequency would then be

a correspondingly smaller fraction of the vibration frequency. That such a relationship should exist seems not at all unlikely. All we have to postulate is that when the carbon atoms are in one or other of their extreme phases as regards distance from the centre of the molecule the CH rotation and vibration are also in extreme phases. We have tried to represent a possible system of this sort in the diagram. The hydrogen of atom 1 is shown at extreme proximity to carbon, and in atom 2 at extreme remoteness, while the CH rotation has undergone half a revolution.



There may have been several CH rotations or vibrations during the epoch in which the carbon atom has undergone the translational change of phase indicated, but at least it seems only reasonable, if symmetry is to be preserved, to suppose that a whole number and one-half of such rotations and vibrations have taken place. There must then be a simple numerical relationship between the two frequencies.

It will not be necessary to deal in detail with the aliphatic hydrocarbon derivatives of benzene. In the preceeding paper it have been shown that the spectra are generally a mixture of types which we may now term the C=C and C-H varieties.

Naphthalene and Anthracene Spectra.

Both ultra-violet absorption and fluorescence of naphthalene exhibit long series of bands at 474 unit intervals. This shows that the spectrum is of the C=C or ethylene type, and little trace of CH influence can be found.

Anthracene bands are at intervals of 1420 or 3×473 and therefore of the same type, but the spectrum is much less sharp than with benzene or naphthalene. It will be noticed that each stage in the condensation of nuclei has produced a three-fold increase in the frequency connected with the double bond. In condensing ethylenic groups to benzene a three-fold decrease occurs. This may be paralleled with the chemical reactivity of the double bond which is of course greatly modified in the case of benzene. But on increasing the number of conjugated bonds as in naphthalene and anthracene the frequency again rises, and to some extent the character of the ethylene bond is restored, *e.g.* naphthalene and anthracene are more readily hydrogenated or halogenated than benzene.

The C=O Vibration.

It has been found that substances which give the strongest "blue bands" contain a C=O group, though the converse is not true. No emission spectrum has been detected from salicylic or cinnamylaldehydes whilst methyl salicylate gave a perfectly continuous spectrum. The view of Coblentz with regard to the origin of the corresponding infra-red band at or about 5.8μ is that "it is not to be found except in those substances containing a CH_3 group and in benzaldehyde. Whether this band is due to CH_3 or some other group vibrating like a CH_3 group is a pertinent question." Examination of the work of Coblentz, however, will show that it is entirely absent in ethane, and it is never strong in aliphatic hydrocarbons, though it certainly does often appear as a minor band. On the other hand it is the strongest band in the acetone spectrum, and is always strong in the aliphatic acids of which a considerable number were examined, and is strong also in the two esters investigated. Among aromatic substances it is very strong in benzaldehyde and cuminal, the only two aldehydes examined. It is also strong in benzoic acid (Spence, *Astrophysical Jour.* xxxix. p. 243, (1914)) and in phenyl acetic acid. Traces of it were found in other aromatic substances, notably eucalyptol and safrol. It will be seen that whilst Coblentz' statement is correct it appears more reasonable to consider the carbonyl group as the most powerful influence making for the production of this band. Further evidence pointing to this conclusion may be drawn from the work of Spence (*loc. cit.*), who made a study of the infra-red absorption spectra of certain alkaloids. He found this 5.8μ band in a number of

instances, whilst it was definitely absent in others. Examples of these classes are given below.

Strong infra-red band at 5.8μ .

Pilocarpine.
Atropine.
Cocaine.
Homatropine.
Narcotine.

No Infra-red band at 5.8μ .

Nicotine.
Quinine.
Quinoline.
Codeine.
Cinchonidine.

All the alkaloids in the list showing the band contain a CO group, whilst none of the substances in the other list have such a group. This is strong evidence that this band in the infra-red is closely connected with the presence of a CO group.

An observation made in an experiment on benzene is also of interest in this connexion. When the vapour of benzene-alcohol mixtures was submitted to the Tesla discharge blue bands were observed, but benzene alone did not give them. The explanation would seemingly be that with alcohol present there is introduced a source of oxygen which under the influence of the Tesla discharge may react to give compounds having a blue band spectrum.

As both in the infra-red and Tesla spectra substances which *should* contain no oxygen have been found to give to a greater or less extent the 5.8μ or "blue bands" it is, perhaps, premature to state dogmatically that these bands have a CO origin, though this is the belief of the writer *. Three classes of vibrations producing banded spectra will then be recognised, due respectively to CH, C=C, and CO bonds.

In conclusion I desire to express my best thanks to all those with whom I have been in collaboration in the previous work, which has here been under review, and more especially to Prof. A. W. Stewart and Mr. W. H. McVicker, whose initiative and skill have been larger contributions to it than my own.

Abstract.

From a consideration of a parallel between the infra-red band intervals of ethylene and the ultra-violet band intervals of benzene, naphthalene, and anthracene, the bands exhibited by these substances are considered to originate in a C=C bond. Similarly the band intervals of type (2) of the preceding paper are shown to originate in a CH bond.

* After very careful purification several of the anomalous substances have now been found to lose all trace of a blue band spectrum.

Benzene also shows vibrations having this origin, and the spectrum is accounted for as a combination of C=C and CH vibrations. It is considered most probable that the "blue band" type of spectrum originates from a carbon-oxygen bond and evidence on this point is brought forward. A view of the benzene molecule is taken accounting for the fact that the bands originating from the two carbon atoms of the C=C bonds show evidence of their being in a state of mutual rotation, whilst the CH groups appear to have a rotation frequency of which their vibration frequency is an exact multiple. This is necessitated if the symmetry of the molecule is to be preserved.

CXXII. *On the Polarization of the Light scattered by Organic Vapours.* By A. S. GANESAN, M.A.*

1. *Introduction.*

IT is well known that the imperfection of polarization of the light scattered by gases and vapours observed in a direction perpendicular to the incident beam largely depends on the nature of the scattering substance. For example, in the case of the monatomic gases, argon and mercury vapour, the transversely scattered light is almost perfectly polarized†; in the case of hydrogen the imperfection of polarization, as measured by ρ , the ratio of the weak component to the strong component in the scattered light, is 3.8 per cent.‡, and for carbon dioxide it is 11 per cent.‡. It is not, however, in general, true that the imperfection would increase with the number of atoms in the molecule; for it is found that in the vapour of ether or pentane, whose molecules contain 15 and 17 atoms respectively, ρ is only about 3 per cent., while in the case of the tri-atomic carbon disulphide it is as great as 16.7 per cent. In order to clear up the problem of the relation that exists between the polarization of the scattered light and the structure of the molecule, it was felt that it would be useful to make a systematic study of the scattering by a series of closely related compounds. In this paper are given the results of experiments made on the vapours of the following series of organic compounds:—the paraffins, some

* Communicated by Prof. C. V. Raman, F.R.S.

† Lord Rayleigh, Proc. Roy. Soc. xcviii. p. 64; cii. p. 190.

‡ *Ibid.* Raman & Rao, Phil. Mag. xlv. p. 433 (1923). Cabannes & Granier, *Journ. de Phys.* iv. No. 12, p. 429.

monohydric alcohols, the chlorine substitution products of methane, benzene and its derivatives, some esters like formates and acetates, and the ketones.

2. *Experimental Arrangements.*

The vapour was contained in an iron cross-tube similar to the one used by Lord Rayleigh and subsequent experimenters, but of more ample dimensions, the inner diameter of the tube being 8 cm. The three short arms, measuring 30 cm. each, were fitted with plane glass windows placed between asbestos rings and held tight by screw-caps. The fourth arm, which was 60 cm. long, was closed at the farther end and contained an obliquely placed green-glass bottle (with its bottom cut off) which formed an efficient background reflecting no light towards the centre of the cross. Sunlight concentrated as described below was admitted through one of the windows, and the scattered light was observed in a perpendicular direction through the other against the black background. At the end of the exit arm was placed a black combination of several colour-filters inclined at 45° so that no light was reflected back. This combination though black was transparent enough to show the direction of the incident beam, which was always kept steady. Apertures of about 3 cm. diameter were placed along the arms at convenient places so as to cut off all stray light. The tube was fairly air-tight, and since in the experiment a continuous stream of vapour was kept passing, it was not found necessary that it should be perfectly air-tight. The cross-tube was wrapped up in a layer of asbestos sheet over which was uniformly wound a coil of nichrome wire which carried a current. The tube could thus be electrically heated and maintained at any desired temperature.

As pointed out by Lord Rayleigh, there was some difficulty regarding the blackening of the interior of the cross-tube. A preliminary experiment was conducted with no painting, but the track was so unsatisfactory that reliable measurements could not be made. Several paints were tried, but some of them were acted upon by the organic vapours, while the others did not stand a high temperature. Finally, the following method was found to satisfy the requirements. The inside of the tube was coated with a solution of sulphur in turpentine and heated with the burner till all the turpentine had evaporated. A smooth black coating of iron sulphide was formed which was not acted upon by the organic vapours.

The three conditions that are necessary to make the scattering by gases and vapours a conspicuous phenomenon,

and to render visual observations to be made accurately, are: (1) an intense source of illumination, (2) a perfectly black background, and (3) an arrangement to shield the observer's eyes from all extraneous light.

The objective of an astronomical telescope of 18 cm. aperture and 200 cm. focal length was fed with sunlight reflected from a large plate-glass mirror. An auxiliary lens of 30 cm. focal length, placed beyond the focus of the object-glass and close to the entrance arm of the cross-tube, focussed the light at the centre of the tube. An intense beam of illumination was thus secured. The observer located himself in a light-tight wooden cage of 4 feet square and 8 feet high. In one of the walls of the cage and at the same vertical height as the centre of the cross-tube was an aperture of about 4 cm. diameter through which the illuminated track could be viewed.

The imperfection of polarization was measured with a double-image prism and nicol. The prism was placed between the observation window of the cross-tube and the aperture of the cage, and adjusted to give two images of the illuminated track in the same horizontal line and just side by side with each other. The stronger track corresponds to vibrations perpendicular to both the incident and scattered beams, while the weaker track corresponds to vibrations parallel to the incident beam. The ratio (ρ) between the intensities of these two components (which is a measure of the polarization of the scattered light) was determined by means of a nicol which could be rotated and whose position could be read on a graduated circle. The combination of the nicol and the graduated circle was fixed inside the observer's cage at the aperture in the wall. The two positions of the nicol for which the two tracks were of the same intensity were found, and if the angle between these two positions be denoted by 2θ then ρ is given by $\tan^2 \theta$. The double-image prism was enclosed in a long black cylindrical tube leading from the cross-tube to the aperture. The tube was covered with several layers of black cloth to make it light-tight. With these arrangements the observer could see only the two tracks and visual observations could be made with a high degree of accuracy.

3. *Supply of Vapour and Procedure.*

For accurate work it is essential that the vapour must be pure and free from dust. In all cases Kahlbaum's chemicals were used. The liquid was evaporated from a glass retort and the vapour was made dust-free by passage through a

tube packed with clean, dry cotton-wool. The tube was electrically heated and maintained at the temperature of the cross-tube by passing a current through a coil of nichrome wire wound round it. The cross-tube was previously made dust-free and heated to a temperature slightly above the boiling-point of the liquid whose vapour was under investigation. When the vapour had passed through for about fifteen minutes it drove away all the air, and the scattering by the pure vapour was observed. The track was well-defined and intense, and measurements were made only when it had been ascertained that there was no dust or formation of clouds. Any tendency to develop a cloud under the action of light could easily be detected. The track instead of being blue became distinctly white, and in some cases was of a streaky nature; the readings showed wide variations with time. In such cases the difficulty was overcome by limiting the illumination to just the time necessary to take a reading. In each case more than 30 readings were taken. After experimenting with each vapour, the cross-tube was heated to a high temperature and a strong blast of filtered air was passed through for about half an hour till all the vapour had been removed. The retort was thoroughly cleaned and dried and the cotton plug was renewed.






4. Experimental Results.

| Substance. | Formula. | Intensity of weak Intensity of strong component in per cent. |
|-----------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| <i>The Paraffins and unsaturated Hydro-carbons.</i> | | |
| Pentane | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ | 3.4 |
| Hexane | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ | 3.3 |
| Heptane..... | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ | 3.1 |
| Octane..... | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ | 2.7 |
| β -iso-amylene (trimethylethylene) } | $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} = \text{CH} \cdot \text{CH}_3$ | 6.1 |

Alcohols.

| | | |
|----------------------|-------------------------------------------------------------------------------------------------------------|-----|
| Methyl alcohol | $\text{CH}_3 \cdot \text{OH}$ | 2.7 |
| Ethyl alcohol | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{OH}$ | 1.7 |
| n. Propyl alcohol } | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ | 2.0 |
| Iso-Propyl alcohol } | $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{CH} \cdot \text{OH}$ | 1.9 |
| n. Butyl alcohol } | $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ | 2.8 |
| Iso-Butyl alcohol } | $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ | 1.8 |
| Allyl alcohol..... | $\text{CH}_2 = \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ | 5.2 |

Benzene and its derivatives.

| | | |
|----------------------|-----------------------------------------------------------------------------------|-----|
| Benzene |  | 6.6 |
| Toluene |  | 6.4 |
| Meta-Xylene |  | 6.7 |
| Chloro-benzene |  | 7.8 |
| Bromo-benzene |  | 7.8 |

Formates and Acetates.

| | | |
|----------------------|-------------------------------------------------------------------------------------|-----|
| Methyl-formate | $\text{O}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{O}-\text{CH}_3$ | 4.6 |
| Ethyl-formate | $\text{O}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{O}-\text{C}_2\text{H}_5$ | 3.6 |
| Propyl-formate | $\text{O}=\overset{\text{H}}{\underset{ }{\text{C}}}-\text{O}-\text{C}_3\text{H}_7$ | 3.5 |
| Methyl-acetate | $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_3$ | 4.8 |
| Ethyl-acetate | $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_2\text{H}_5$ | 4.4 |
| Propyl-acetate | $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_3\text{H}_7$ | 3.2 |

Chlorine substitution products of Methane.

| | | |
|----------------------------|-----------------|-----|
| Chloroform | CHCl_3 | 3.2 |
| Carbon tetrachloride | CCl_4 | 1.9 |

Ketones.

| | | |
|----------------------------|-----------------------------------------------------------------------------------|------|
| Dimethyl ketone | $\text{O}=\text{C} \begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$ | 4.8 |
| Methyl-ethyl ketone | $\text{O}=\text{C} \begin{cases} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{cases}$ | 4.4 |
| Methyl-propyl ketone | $\text{O}=\text{C} \begin{cases} \text{CH}_3 \\ \text{C}_3\text{H}_7 \end{cases}$ | 3.2 |
| Carbon disulphide | $\text{S}=\text{C}=\text{S}$ | 16.7 |
| Ether | $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$ | 3.2 |

5. Comparison with previous measurements.

S expressed as a percentage.

| Substance | Rayleigh [*] | Raman and Das [†] | Author |
|----------------------|-----------------------|----------------------------|--------|
| Petroleum | 1.2 | 1.4 | 84 |
| Benzene | 2.1 | 2.2 | 84 |
| Chloroform | 3.4 | 3.6 | 82 |
| Carbon tetrachloride | 3.5 | 3.5 | 79 |
| Carbon disulphide | 11.0 | — | 107 |
| Water | 1.7 | 1.9 | 82 |

6. Discussion of Results.

At this stage it is perhaps premature to attempt a detailed discussion of the relation between the structure of the molecule and the polarization of the light scattered by it. Experiments have also been made on the scattering of light in organic liquids by Mr. H. S. Krishnan in this laboratory, and when these data have been published it is proposed in a joint paper, to discuss the problem in detail. But based on the experimental values quoted above, some interesting facts may be mentioned.

In the paraffin series of compounds, as we pass from petroleum to octane, the molecules become longer, and if we associate optical anisotropy with anisotropy of shape, we might expect an increasing optical anisotropy as we go up the series. But from the values given above, it is clear that there is no such increase in the depolarization; if anything, there is a tendency for an actual decrease in the value.

Another interesting fact is that whenever we have a "double bond" in the structure of the molecule, we have a high value for the "factor of depolarization." This is to be seen in the case of the unsaturated hydro-carbon amylenes, which has a value nearly twice that for the paraffin series; and also in the case of allyl alcohol, where the depolarization is much greater than for the mono-hydric alcohol. The *iso*-compounds show a smaller optical anisotropy than the normal ones.

The benzene series affords a very interesting study. The three homologues benzene, toluene, and xylene show the

* Strutt, Proc. Roy. Soc. xcv. p. 155.

† Phil. Mag. xlv. (March 1923): xlv. (Sept. 1923).

‡ R. Venkateswara, Trans. Chem. Soc. xlv. p. 1933 (1921).

same degree of imperfection, namely 6.5 per cent. This may be explained as due to the predominating influence of the closed chain of the six carbon atoms, the hydrogen or its substitution by an alkyl radicle exerting little or no influence on the optical anisotropy of the molecule.

The methyl compounds always show a greater imperfection of polarization than the ethyl ones. This is to be seen not only with the formates, acetates, and alcohols but also with the ketones, where dimethyl ketone containing two methyl radicles shows a greater value for ρ than the other two compounds.

As is to be expected, the more symmetrical molecule CCl_4 shows a smaller value for ρ than chloroform CHCl_3 . Experiments are in progress to investigate the effect of successive replacements of H by Cl in CH_4 .

In conclusion, I have much pleasure in recording my indebtedness to Professor C. V. Raman for the great interest he took in the experiments, which were conducted at the Physical Laboratory of the Indian Association for the Cultivation of Science.

Calcutta,
26th June, 1924.

CXXIII. *On some Chemical Deposits of a Regular Form.*

By J. M. MULLALY, B.A., War Memorial Student in Natural Science, Balliol College, Oxford.*

THE deposits are those of the salt ammonium chloride obtained by the steady diffusion through one another of ammonia and hydrogen chloride in a glass tube of uniform bore. A medium of air was present in the tube.

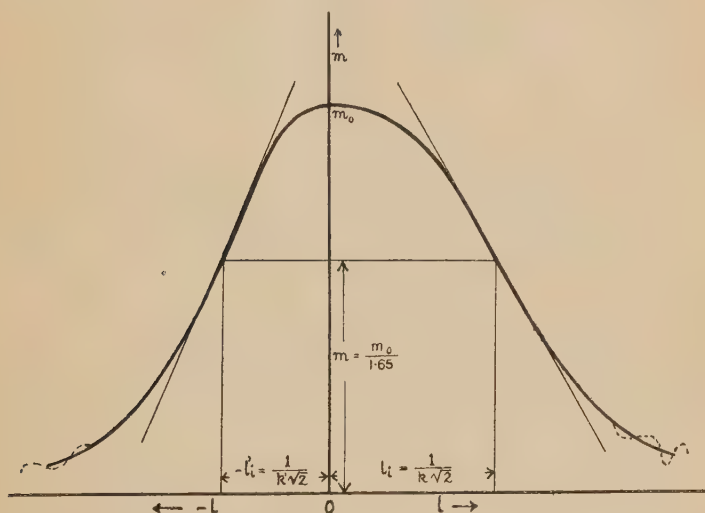
The object has been to find experimentally the law of distribution of deposit along the axis of the tube, that is, to find the curve representing the mass of salt condensed in a given time per unit area of the tube wall at different points.

The means employed was the direct estimation of thickness by means of a travelling microscope focussed on the crystals from the exterior, and radially to the walls, which have been cleared of deposit on the nearer side. Refraction by the glass did not, of course, distort the deposits in the line of the axis. The precision attained was sufficient on a thickness of 0.1 to 2 mm.

* Communicated by the Author.

It would seem that the distribution may be represented by the combination of two error curves, with a common origin at the point on the axis where the deposit is thickest.

Let the axis be regarded as positive on the side from which ammonia diffuses, and negative on that from which the hydrogen chloride diffuses.



Then the curves are

$$m/m_0 = e^{-k^2 l^2} \text{ in the positive region,}$$

and $m/m_0 = e^{-k'^2 l^2}$ in the negative region.

k and k' are constants in a given tube. m_0 is the maximum value of m where $l=0$.

The curves terminate at the sources of the two combining gases, and thus extend over a region fixed arbitrarily by the positions of these sources upon the axis.

The experiments were as follows :—

| l , in mm. | Thickness in mm. | $k^2 = -\frac{2.303}{l^2} \log_{10} \frac{m}{m_0}$ in mm. ⁻² . |
|-----------------|---------------------|------------------------------------------------------------------------------|
| 0 | 1.20 (m_0) | |
| 0.25 | 1.13 | 0.50 |
| 0.50 | 1.08 | 0.45 |
| 0.75 | 0.89 | 0.53 |
| 1.00 | 0.73 | 0.50 |
| 1.50 | 0.37 | 0.46 |
| 2.00 | 0.19 | 0.52 |

To determine k (or similarly k') it is most convenient to locate upon the axis of the tube the corresponding point l_i of inflexion at which

$$\frac{d^2m}{dl^2} = -2m_0k^2e^{-k^2l^2}(1-2k^2l^2) = 0.$$

Hence $1 - 2k^2l_i^2 = 0,$

or $k = \frac{1}{l_i\sqrt{2}};$

similarly $k' = \frac{1}{l_i'\sqrt{2}},$

where l_i' locates the point of inflexion in the negative region. Negative values of k and k' are inadmissible.

The points of inflexion can readily be seen without optical aid; and occur where $m = \frac{m_0}{\sqrt{e}} = \frac{m_0}{1.65}.$

As the deposit grows from moment to moment, the values of k and k' do not change. Again, other things being equal, these constants are unchanged whether the tube be narrow or whether it be wider, if not much exceeding the usual quill size.

The magnitudes of k and k' for a given length of tube may vary within extremely wide limits according to the temperature and other circumstances, *e. g.* the nature of the sources of the vapours. But such circumstances are here considered alike for all the tubes.

For comparison of various tubes, k and k' may well be referred to the respective distances L and L' of the two sources (ammonia and hydrogen chloride) from the origin.

| Tube. | L. | L'. | $k.$ | $k'.$ | $kL.$ | $k'L'.$ |
|---------|--------|------|------------------------|-------|-------|---------|
| | in mm. | | in mm. ⁻¹ . | | | |
| 1 | 770 | -256 | 0·7 | 1·0 | 540 | -256 |
| 2 | 369 | -127 | 1·6 | 2·1 | 590 | -266 |
| 3 | 670 | -218 | 0·9 | 1·2 | 600 | -262 |

It is evident that kL and $-k'L'$ are numerical constants having the values 560 and 260 under the chosen circumstances. This indicates the fact that $\frac{l_i}{L}$ and $\frac{l_i'}{L'}$ are constants under the given conditions, which is easily imagined since the diffusion occurs in a steady state.

As sources of the gases aqueous hydrochloric acid of 7.7 N strength, and ammonium hydroxide of 0.49 N strength, were used, being chosen somewhat at random. The tubes were kept at a temperature of 25° C. in a thermostat.

A stream of water vapour diffused through these tubes from the side containing ammonia to that containing the acid. This does not cause a change in the form of the law, though it influences the values of the constants.

It might be mentioned that in the outer fringes of the deposits were sometimes to be seen faint rings and bands of the salt.

I desire to record my indebtedness to Dr. J. W. Nicholson for proposing to me the problem.

31 Linton Road,
Oxford.
11th February, 1925.

CXXIV. *The Crystal Structure of Lithium Potassium Sulphate.* By A. J. BRADLEY, M.Sc., Ph.D., *The Physical Laboratories, University of Manchester* *.

1. *The Marshalling of the Structure.*

LITHIUM potassium sulphate and the isomorphous lithium rubidium sulphate are the only two simple hexagonal sulphates known, and it therefore seemed possible that an investigation of their structure might be comparatively easy and would yield valuable information. LiKSO_4 has an axial ratio $c:a=1.6755:1$ and a density 2.393 †. Its symmetry is hexagonal polar C_6 , and is very well established by the general physical properties of the crystal and, in particular, by etch figures.

The method of investigation was originally the powder photograph, only very small crystals being then available. The apparatus and experimental methods have been described previously ‡. The spacings calculated from mean measurements of two films (Table I., Col. I.) fit on Hull and Davey's graph for a simple hexagonal lattice of axial ratio $1.675:1$, in good agreement with the crystallographic data. From these measurements, the volume of the unit cell which is a rhombic prism is 195.5×10^{-24} c.c. From the crystallographic data, the volume containing one molecule LiKSO_4 is 98.0×10^{-24} c.c., so that there are two molecules to the unit cell. The theoretical spacings for a structure consisting of a simple hexagonal lattice with two molecules to the unit cell are given in Col. II.

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† Groth, *Chemische Krystallographie*, ii. p. 329.

‡ Phil. Mag. xlvii. p. 657 (1924).

TABLE I.

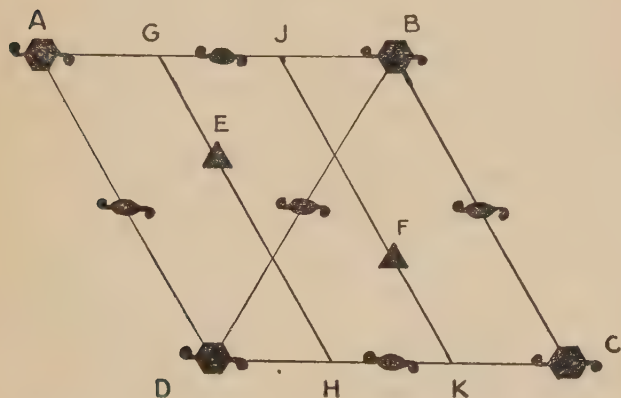
| I. | II. | III. | IV. | V. |
|-----------------------|------------------------|---------|--------------------|-------------------|
| $\frac{d}{n}$ (obs.). | $\frac{d}{n}$ (calc.). | hkl . | Intensity (calc.). | Intensity (obs.). |
| ... | 8.60 | 0001 | ... | ... |
| ... | 4.445 | 1010 | 5 | ... |
| ... | 4.300 | 0002 | 26 | ... |
| 3.94 | 3.950 | 1011 | 217 | v.s. |
| 3.09 | 3.090 | 1012 | 216 | v.s. |
| ... | 2.867 | 0003 | ... | ... |
| 2.566 | 2.565 | 1120 | 120 | v.s. |
| 2.423 | { 2.458 | 1121 | 73 | w. |
| | { 2.408 | 1013 | 15 | |
| | { 2.220 | 2020 | 17 | v.s. |
| 2.186 | { 2.204 | 1122 | 158 | |
| | { 2.150 | 0004 | 70 | |
| | { 2.148 | 2021 | 16 | |
| 1.970 | { 1.973 | 2022 | 56 | f.s. |
| 1.912 | { 1.936 | 1014 | 31 | |
| | { 1.912 | 1123 | 29 | |
| ... | 1.754 | 2023 | 1 | ... |
| ... | 1.720 | 0005 | ... | ... |
| ... | 1.679 | 2130 | 11 | ... |
| 1.642 | { 1.649 | 1124 | 52 | s. |
| | { 1.648 | 2131 | 28 | |
| 1.595 | 1.604 | 1015 | 21 | v.w. |
| 1.560 | 1.563 | 2132 | 130 | s. |
| ... | 1.544 | 2024 | 35 | ... |
| 1.481 | 1.481 | 3030 | 89 | s. |
| ... | 1.460 | 3031 | 0 | ... |
| ... | 1.450 | 2133 | 3 | ... |
| ... | 1.433 | 0006 | 3 | ... |
| ... | 1.429 | 1125 | 9 | ... |
| ... | 1.401 | 3032 | 9 | ... |
| 1.367 | { 1.364 | 1016 | 29 | w. |
| | { 1.361 | 2025 | 13 | |
| 1.324 | 1.323 | 2134 | 30 | v.w. |
| ... | 1.315 | 3033 | 0 | ... |
| 1.286 | 1.282 | 2240 | 32 | v.w. |
| ... | 1.268 | 2241 | 1 | ... |
| 1.253 | 1.251 | 1126 | 66 | m. |
| ... | 1.232 | 3140 | 9 | ... |
| ... | 1.229 | 0007 | ... | ... |
| ... | 1.229 | 2242 | 22 | ... |
| 1.223 | { 1.220 | 3034 | 59 | f.s. |
| | { 1.220 | 3141 | 18 | |
| 1.201 | { 1.203 | 2026 | 17 | v.w. |
| | { 1.201 | 2135 | 17 | |
| 1.187 | { 1.185 | 1017 | 4 | m. |
| | { 1.183 | 3142 | 70 | |


v.s. = very strong ; s. = strong ; f.s. = fairly strong ;
m. = medium ; w. = weak ; v.w. = very weak.



The powder photograph shows that there is no reflexion corresponding to (0001), (0003), or (0005), and this was confirmed by measurements made later on a single crystal by the spectrometer. A definite reflexion from (0002) can be observed by the spectrometer, though nothing is visible on the photograph.

The only space-group of symmetry C_6 for which the spacing (0001) is halved is C_6^2 . There are also two other space-groups of higher symmetry which fulfil the same condition, namely C_{6h}^{12} and D_6^6 . These possess all the symmetry elements of C_6^2 in addition to certain extra elements, and therefore any space-group to which LiKSO_4 belongs must possess at least all the symmetry elements of C_6^2 , which are shown in fig. 1.

Fig. 1.



 represents a hexagonal screw axis of translation $\frac{c}{2}$,

 a threefold rotatory axis, and  a twofold screw axis. These are the only elements of symmetry of C_6^2 . A B C D represents a projection of the unit cell perpendicular to the hexagonal axes. Within this cell we have to place six ions, namely two each of K, Li, and SO_4 . In order to preserve the symmetry these ions must go at the four corners A, B, C, D or at E and F, the centres of triangles ABD, DBC respectively. If any ion is placed at A, the other ion of the same type will also be placed at A. If any ion is placed at E, the corresponding ion will be placed at F, and *vice versa*.

The arrangement of the oxygen atoms in the sulphate ion is determined by the symmetry of the crystal. Three of

these atoms must be equidistant from the sulphur atom, and must lie in a plane perpendicular to the hexagonal axes of the structure. The fourth will lie so that the same hexagonal or trigonal axis passes through both it and the sulphur atom. Its distance from the sulphur atom will probably be different from that of the other three oxygen atoms, as its environment will be quite different; but, as will be shown later, the difference is too small to measure.

There are two possible positions for these sulphate ions: they may both be placed at A, or one may be placed at E and one at F. Intensity considerations alone can decide between these two structures. An examination of the powder photograph shows that the $(10\bar{1}0)$ plane gives no visible first-order reflexion, but a large third order. This must mean that the reflecting atoms are concentrated on planes AD, GH, JK, so that the reflecting power of each plane is almost the same; and hence if the sulphate ions are at A, the potassium ions are at E and F, and *vice versa*. The strongest line on the film is due to the plane $(10\bar{1}2)$. It is therefore necessary to find a structure which gives only a minute $(10\bar{1}0)$ reflexion and a strong $(10\bar{1}2)$ reflexion.

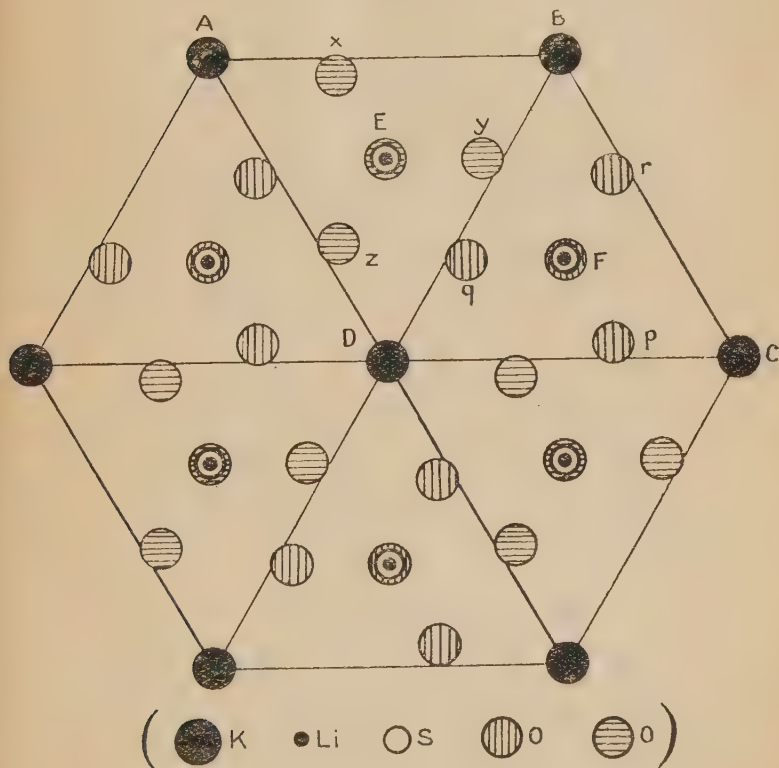
It can easily be shown that any arrangement in which the sulphate ions are situated at A is impossible. They would completely outweigh the K and Li atoms at E and F, unless their oxygen atoms were so far from the sulphur atoms that the former reinforced the planes GH and JK, and were quite out of phase with the plane AD. On the other hand, if the sulphate groups are at A, a strong $(10\bar{1}2)$ reflexion will only be obtained if the oxygen atoms are crowded close to the centre of the sulphate ion. This is impossible, and therefore the sulphate ions are placed at E and F. In order to compensate these ions, it is necessary to put heavy atoms in the plane AD. The potassium atoms are therefore situated at A. The position of the lithium atoms cannot be fixed by X-rays, as they have an almost negligible effect on the intensity of the spectra; considerations of space and the distribution of positively- and negatively-charged ions indicate that they are situated at E and F.

The structure is shown in fig. 2, which is a projection perpendicular to the hexagonal axis. Potassium atoms are situated at A, and sulphur, lithium, and one oxygen atom at each of E and F. The remaining six oxygen atoms are at x, y, z, p, q, r . So far there are two parameters—the distance Ex and the angle FEx . The orientation of the second sulphate ion $Fpqr$ is then fixed by symmetry. The

angle EFq is equal to the angle FEy , and FP is equal to Ex . This structure possesses no planes of symmetry parallel to the hexagonal axis unless $FEy = 0^\circ$ or 60° .

Fig. 2.

$\langle \dots \dots 5.13 \text{ \AA} \dots \dots \rangle$



2. The Evaluation of the Parameters.

A. Two parameters at right angles to the hexagonal axis.

The two parameters which fix the angle FEy (fig. 2) and the distance Ex can be found approximately by a study of planes parallel to the hexagonal axis. The angle ϕ (FEy) may vary between 0° and 120° , but values 60° and 120° are indistinguishable by X-rays from those between 60° and 0° . As the structure of a sulphate had never been completely elucidated, there was no estimate obtainable of size of the SO_4 group; but it may be possible to get some idea of what

is a likely value for Ex by a consideration of the CO_3 group, which is one of the few complex acid radicles which have been fully investigated hitherto. In calcite the distance carbon to oxygen is 1.3 \AA . The mutual repulsion of the oxygen atoms is overcome by the big charge on the carbon atom. It is probable that the oxygen atoms are drawn practically as close together as they can ever be. In the present instance they will tend to be pulled in further by the greater charge on the sulphur atom, but the greater size of the sulphur ion and the increased repulsion due to the extra oxygen atom will act in a reverse manner. It is therefore reasonable to suppose that the distance Ex lies between 1.2 \AA and 1.7 \AA .

For the purpose of evaluating these parameters, reflexions were obtained from the face $(10\bar{1}0)$ of a single crystal, using the X-ray spectrometer, with molybdenum radiation. The values obtained for the various orders of reflexion are given in Table II., Col. II.

TABLE II.

| I. hkl . | II. Observed intensities. I. | III. Structure factor. A. | IV. $\frac{I}{A^2}$. | V. Scattering power of oxygen. |
|---------------|---------------------------------------|------------------------------------|--------------------------|--------------------------------------|
| 0001 | ... | ... | ... | ... |
| 10 $\bar{1}0$ | 9.5 | 2.1 | 2.15 | 10.0 |
| 0002 | 65.5 | 8.3 | 0.95 | 10.0 |
| 0003 | ... | ... | ... | ... |
| 11 $\bar{2}0$ | 87.4 | 17.4 | .29 | 7.3 |
| 11 $\bar{2}1$ | 27.5 | 10.0 | .275 | 7.0 |
| 20 $\bar{2}0$ | 18.5 | 7.5 | .33 | 6.5 |
| 0004 | 167.0 | 27.5 | .22 | 6.3 |
| 11 $\bar{2}3$ | 7.4 | 8.2 | .11 | 5.7 |
| 0005 | ... | ... | ... | ... |
| 30 $\bar{3}0$ | 62.5 | 26.0 | .092 | 4.3 |
| 0006 | 8.8 | 9.2 | .10 | 4.0 |
| 11 $\bar{2}5$ | 3.9 | 5.9 | .11 | 4.0 |
| 40 $\bar{4}0$ | 1.8 | 5.3 | .064 | 2.0 |
| 11 $\bar{2}7$ | 0.3 | 2.8 | .04 | 2.0 |
| 50 $\bar{5}0$ | 0.45 | 7.6 | .008 | ... |
| 60 $\bar{6}0$ | 3.5 | 19.0 | .010 | ... |
| 90 $\bar{9}0$ | 0.5 | 19.0 | .001 | ... |

The relative values of the observed intensities for $(10\bar{1}0)$ and $(30\bar{3}0)$ confirm the deductions made from the powder photograph for the marshalling of atoms in planes parallel to $(10\bar{1}0)$. Structure factors for the various orders of reflexion

from $(10\bar{1}0)$ were calculated for various values of ϕ between 0° and 60° , and of E_x between 1.2 and 1.7. Whatever reasonable assumptions be made as to the relative scattering powers of the different atoms, calculation shows that for almost any values of the parameters within the above limits the reflexion from $(10\bar{1}0)$ will be weak, but that from $(30\bar{3}0)$ will be strong. From the observations made by the spectrometer it is clear that the structure factor of $(20\bar{2}0)$, which alters rapidly with a change in ϕ , must be of an intermediate size. This can only be the case if ϕ has a value round about 30° , say between 25° and 35° , and its precise value can be fixed very accurately if we know the exact value of E_x . A comparison of the intensities $(10\bar{1}0)$, $(20\bar{2}0)$, and $(30\bar{3}0)$ with that of $(11\bar{2}0)$ shows that the plane $(11\bar{2}0)$ must have a structure factor intermediate between that of $(20\bar{2}0)$ and $(30\bar{3}0)$. This is actually the case if ϕ is about 30° , unless E_x is very small. Any value greater than about 1.3 Å is admissible. If $E_x = 1.4$ Å, ϕ must be almost exactly 30° ; and this seems to be the most reasonable value to choose for E_x , for any appreciably larger value brings oxygen atoms of neighbouring SO_4 groups too close together.

The positions of the oxygen atoms in fig. 2 have now been determined. From a consideration of the reflexions from planes parallel to the hexagonal axis, the angle FF_2 is about 30° , and the distance E_x is not less than 1.3 Å. Spatial considerations indicate that it is not greater than about 1.5 Å.

B. Parameters parallel to the hexagonal axis.

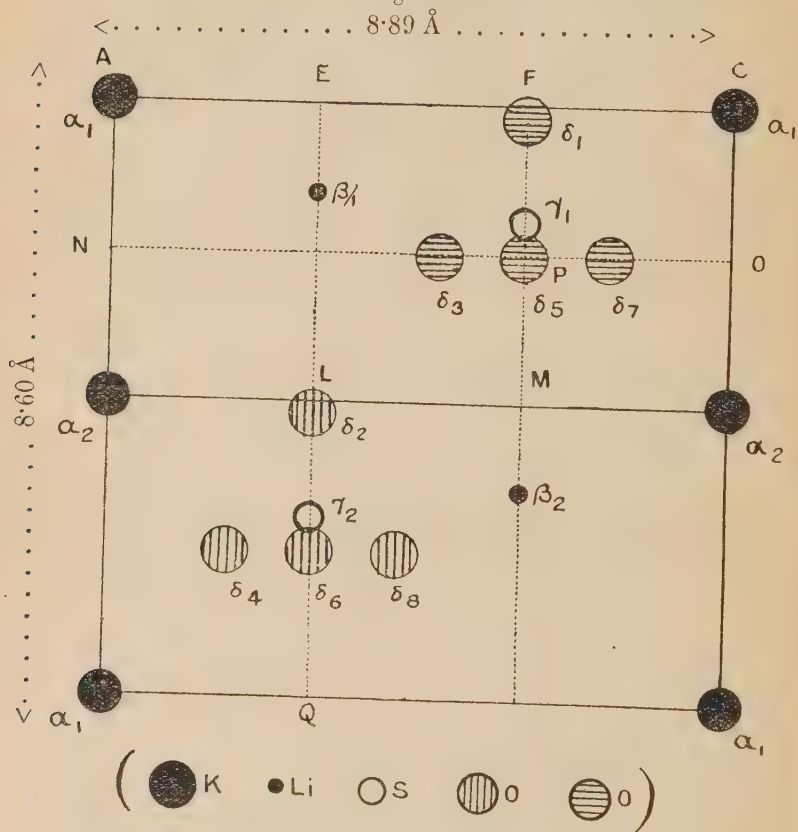
The distribution of atoms along the hexagonal axis can be partially determined by a study of the spectra from planes (0001) . All odd orders of reflexion are absent; the ions are therefore arranged in pairs along the hexagonal axis, so that the (0001) spacing is halved. The atoms are arranged in the manner shown in fig. 3. This is a projection of the unit cell through AC parallel to the hexagonal axis. a, b, c, d are potassium, lithium, sulphur, and oxygen atoms respectively.

If we regard the positions of the potassium atoms as fixed, the positions of the lithium and sulphur atoms are determined by the parameters $\text{ES}_1 = \text{MS}_1$ and $\text{FY}_1 = \text{LY}_1$ respectively. In order to fix the positions of all the oxygen atoms four independent parameters must be determined. Two of these have already been fixed. The two remaining parameters are $\gamma_1 \delta_1 = \gamma_1 \delta_2$, which fixes the position of the oxygen atom at δ_1 , and the distance $\gamma_1 \text{P}$ of γ_1 from the line

$\delta_3 \delta_5 \delta_7$, which fixes the position of the other three oxygen atoms.

Of the even orders from (0001), which alone occur, the only strong reflexions are (0002) and (0004), and the second of these is nearly three times as strong as the first. The phase factor for (0004) like that for (30 $\bar{3}$ 0) is therefore

Fig. 3.



very nearly normal. (0006) is quite small. This shows that the atoms are concentrated in planes AC and LM, and also in planes half-way between, NO (fig. 3). The comparatively small reflexion from (0002) requires planes AC and NO to be almost equal in reflecting power. This will be the case if γ_1 , δ_3 , δ_5 , δ_7 are situated close to NO, and δ_1 as well as α_1 is on or near AC. Very little variation in these positions is allowable.

It is reasonable to suppose that the sulphur atom is approximately at the centre of the tetrahedron formed by the surrounding oxygen atoms. In this case $\gamma_1 P = \frac{1}{3} \gamma_1 \delta_1$. Since δ_1 is almost in the plane AC, and P is almost in the plane NO, $\gamma_1 P$ is approximately one-quarter AN, *i. e.* 0.5 \AA . The distance of the odd oxygen atom of the SO_4 group from the central S atom ($\delta_1 \gamma_1$) must be about $1.5\text{--}1.6 \text{ \AA}$; for if it were more, this oxygen atom would approach too close to the nearest oxygen atoms of the next SO_4 groups (*e. g.* δ_2 would be too near δ_3), and if it were less, δ_1 would be too far from the plane AC. This value is exactly the same as the distance of the other oxygen atoms calculated from $Ex=1.4$ and $\gamma_1 P=0.5$; so that, as nearly as one can estimate, the four oxygens of the SO_4 group are situated at the corners of a regular tetrahedron. The position of the lithium atom is somewhat uncertain. β_1 may be anywhere along the line EL. In any case it is likely to be fairly close to the three oxygen atoms such as δ_3 , but it may be either above or below δ_3 . As there is quite a big space in the structure above δ_3 and very little room below, it very likely goes above.

The approximate position of all the atoms in the structure has thus been determined independently of any assumption with regard to the relative extent to which the atoms of different elements scatter radiation at different angles of reflexion. In order to obtain any more precise definition of the parameters and to check the agreement between observed intensities of reflexion and calculated values, it is necessary to make some assumptions. Some information can actually be obtained as to the relative scattering power of oxygen. Planes $(11\bar{2}1)$, $(11\bar{2}3)$, $(11\bar{2}5)$, $(11\bar{2}7)$ have exactly the same phase factor; the Li, K, and S atoms are spaced in pairs in such a way that each atom is exactly out of phase with the other of the same kind. We are therefore dealing with oxygen atoms only, and these are arranged in precisely the same way in each of the four planes.

Reflexions from these planes were obtained by means of the spectrometer (see Table II.). The intensity of reflexion diminishes very rapidly with increasing glancing angle, which shows that the oxygen atoms are very inefficient reflectors at large glancing angles. As a rough approximation, the relative scattering powers of K and S have been assumed to be proportional to the number of electrons in each atom when fully ionized; thus $K=18$, $S=10$. This is probably not far from the truth over most of the range of angles considered here. Perhaps the value of S is rather low,

particularly for large angles. On the other hand, it is clear that the scattering power of oxygen falls off so much more rapidly that it cannot be represented by a constant in the same way. A comparison of the reflexions $(11\bar{2}1)$, $(11\bar{2}3)$, $(11\bar{2}5)$, $(11\bar{2}7)$ with that of $(30\bar{3}3)$ has led to the figures for the scattering power of O relative to S and K, which are given in Table II., Col. V., though of course these are only to be regarded as approximate. These figures have been used to calculate structure factors for all the other planes.

Some allowance has been made for the lithium atoms, but in any case the effect of the lithium atoms is so small as to make no appreciable difference. The uncertainty as to the relative scattering powers of the other three kinds of atom is much more serious, and will certainly give rise to quite large errors.

In consequence, too much reliance cannot be placed on individual agreement or divergences between observed and calculated intensities. Moreover, there is as yet no knowledge of the part played by "extinction" * in reducing the intensity of the stronger reflexions. One can therefore only hope for a rough general agreement between the observed and calculated intensities. The comparison is made the most easily by arranging the planes in descending order of magnitude of spacing. The intensity of reflexion I should be proportional to the product of the square of the structure factor A and a factor which falls off steadily as the glancing angle increases. The quotient $\frac{I}{A^2}$ should therefore show a gradual decrease as we pass from planes with large spacings to those with small spacings. Column IV. shows that this is the case.

This method of comparison was first used by W. L. Bragg † for the case of aragonite, except that he found that the intensity was more nearly proportional to the structure factor itself. This is certainly not the case in the present instance ‡.

The precise value of the parameter $\gamma_1 F$ used for calculating the values of A shown in the table was obtained in the following way. The spectrum from (0006) was quite small, whilst that from $(11\bar{2}6)$ as observed on the powder photograph

* W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.* xlii. p. 1 (1921); C. G. Darwin, *Phil. Mag.* xliii. p. 800 (1922).

† W. L. Bragg, *Proc. Roy. Soc. A*, cv. p. 16 (1924).

‡ Compare G. Greenwood, *Phil. Mag.* xlviii. p. 654 (1924).

was quite appreciable. This is only the case if $\gamma_1 F$ lies about 1.7 \AA . The other values employed were $\phi = 30^\circ$, $E\alpha = 1.4 \text{ \AA}$, $\gamma_1 P = 0.5 \text{ \AA}$, $\gamma_1 \delta_1 = 1.5 \text{ \AA}$, $L\beta_1 = 3.0 \text{ \AA}$.

In order to check by the powder photograph the values allotted to the various parameters, a complete determination was made of the calculated intensities of all the planes down to $(31\bar{4}2)$. The structure factors were calculated in the usual manner; and in each case the square of the structure factor was multiplied by a factor N , which is the number of co-operating sets of planes, and by the angular factors for the powder method. The latter was assumed to be proportional to the square of the cosecant, as in the case of arsenic*. The values calculated by this means are shown in Table I., Col. IV. They may be compared with the observed intensities for the powder photograph shown in Table I., Col. V.

On the whole the agreement is reasonably good, and provides a satisfactory confirmation of the values allotted to the various parameters, which were fixed by the spectrometer method. The factor allowing for the change of the relative scattering power of oxygen was assumed to have the values calculated very approximately from the spectrometer measurements. A large error may be introduced in the calculations of certain reflexions on this assumption. The plane $(11\bar{2}1)$ in particular seems to show this effect.

The Results of X-Ray Analysis.

The structure of LiKSO_4 is shown in projection in figs. 2 and 3. The unit cell is a hexagonal prism of base $AB = 5.13 \text{ \AA}$ and height $EQ = 8.60 \text{ \AA}$. The potassium ions are situated on a simple hexagonal lattice of axial ratio $a:c = 1:0.838$. The sulphate ions comprise two simple hexagonal lattices of axial ratio $a:c = 1:1.6755$, which fit together as if the sulphate ions were spheres in hexagonal close-packing. Lithium ions alternate with sulphate ions. Each sulphate ion has six potassium ions as neighbours, and each potassium ion is surrounded by six sulphate ions.

The oxygen atoms are arranged around the sulphur atom of the sulphate group in tetrahedral fashion. Three oxygen atoms must be equidistant from the central sulphur atom, and the distance of the fourth cannot be much different. The actual distance is found to be $1.5\text{--}1.6 \text{ \AA}$. A model of the structure was made on a scale of 1 \AA to 1 cm. , the atoms being represented as spheres with the following radii:— $K = 1.34$, $Li = 0.79$, $O = 1.36$. These values were

* Phil. Mag. *loc. cit.*

suggested by Prof. Bragg, the values originally proposed by him* being modified in the manner suggested by Wasastjerna†. The model shows oxygen atoms belonging to neighbouring sulphate groups in contact, but there is more space for the potassium and lithium atoms than is actually filled by them.

A remarkable fact is the closeness between the axial ratio of LiKSO_4 (1.6755) and the theoretical value for a system of spheres in close-packing (1.633). In the case of the isomorphous LiRbSO_4 , the value is still closer (1.6472). This suggests that the sulphate group, which is by far the largest entity in the crystal, is the chief factor in deciding the nature and dimensions of the crystal. Viewed in this light, the structure is formed by the closest hexagonal packing of sulphate ions, the latter being roughly spherical in shape.

The size of the unit is thus determined almost solely by the size of the sulphate ions, the metallic ions filling up as far as possible the interstices of the structure. The rubidium or potassium and lithium atoms appear to be nearly the right size for this purpose, the structure being scarcely distorted from the ideal axial ratio. The loose packing of the potassium atoms as shown by the model may arise from the possibility that the sulphate group is not best represented as four separate spheres of oxygen, but that there is, in addition, a sphere of influence due to the sulphate ion as a whole, so that metallic ions are driven away from the hollows between neighbouring oxygen atoms. Such a supposition would explain the remarkable value of the axial ratio, and would show that the metallic atoms are actually packed quite tightly into the structure.

It should be noted that the space-groups C_{6h}^2 and D_6^6 are ruled out by the absence of planes of symmetry in the structure, so that the space-group of the complete arrangement is C_6^6 , in complete correspondence with the crystallographic evidence. The structure possesses enantiomorphism, owing to the asymmetrical arrangement of the oxygen atoms about the hexagonal axes. Thus the parameter ϕ ($\text{Fe}\gamma$, fig. 2) may be either 30° or 90° , the difference between these two arrangements being due to the lack of an equatorial plane of symmetry; but there is no possibility of distinguishing between the two enantiomorphous arrangements by means of X-rays. Wulff and others have, however, found that there are two distinct types of crystal, one of which is *laevo*- and

* W. L. Bragg, *Phil. Mag.*, xli, p. 169 (1920).

† J. A. Wasastjerna, "On the Radii of Ions," *Soc. Scient. Fenn., Comm. Phys.-Math.* i, p. 38 (1923).

the other dextro-rotary, and this would appear to show that crystals exist with either of the two possible values of ϕ . Normally, as Wulff has shown, a lamellar twin is formed by layers of the two types alternating along the optic axis, so that no rotary polarization can be observed. This is precisely what might be expected from the structure. A new layer of SO_4 groups which is deposited on a (0001) face may either fall into the same position as the layer next but one previously, and so make a normal repetition of the structure, or it may commence an enantiomorphous crystal without the slightest distortion of the lattice. In this case a layer of K atoms (*e. g.* $\alpha_2 \alpha_2$ in fig. 3) is common to both twins. In fig. 2 we shall have $\text{EF}q = 120^\circ - \text{FE}\gamma = 90^\circ$, but fig. 3 will be unaltered.

Summary.

The crystal structure of LiKSO_4 consists of a system of sulphate ions in hexagonal close-packing, alternating with metallic ions. The potassium ions form a simple hexagonal lattice, while the lithium ions are arranged like the sulphate groups.

The lattice dimensions were fixed from a powder photograph, the unit cell being a prism of base 5.13 \AA and height 8.60 \AA and containing two molecules of LiKSO_4 . The space-group is C_6^6 .

The parameters fixing the relative positions of the different kinds of atoms were evaluated from intensity measurements made by the X-ray spectrometer. The position of all except the lithium atoms was fixed by this means, the position of the latter being determined by spatial considerations. The sulphate ion is a tetrahedron of oxygen atoms surrounding a central sulphur atom, the distance S-O being $1.5\text{--}1.6 \text{ \AA}$.

I take this opportunity of expressing my thanks to Messrs. R. W. James, M.A., and G. Greenwood, M.Sc., to whom I am indebted for the spectrometer measurements. I desire to thank Prof. W. L. Bragg, F.R.S., and Mr. James for the great interest they have taken in this work and for their advice and guidance. Part of the apparatus used was purchased from money kindly given to the Physical Laboratory by the Government Grant Committee of the Royal Society and by Messrs. Brunner, Mond. During all except the concluding stages of the work the Author was in receipt of a grant from the Board of Scientific and Industrial Research. I wish to thank Messrs. Metropolitan-Vickers for the opportunity of concluding this work.

CXXV. *The Behaviour of Hydrogen in the Discharge due to Alternating Electric Fields of High Frequency.* By R. WINSTANLEY LUNT, M.Sc., Ph.D., 1851 Exhibition Senior Student*.

INTRODUCTION.

ARISING out of a research about to be published elsewhere (Proc. Roy. Soc. May 1925) on the chemical effects in gases produced by coronas due to alternating electric fields of frequency of the order of 10^7 cycles per second, is the question of the incidence of the ionization produced by such fields on the chemical changes which have been observed.

An attempt has now been made to carry out a preliminary investigation of the ionization produced in hydrogen at the frequency 1.5×10^7 .

An analysis of the current voltage relationships occurring in an ozonizer or ionization vessel is put forward, in the light of which, as far as possible, all results will be discussed. Its chief claim to consideration lies in its simplicity compared with that of the only analysis of consequence extant, namely that of Warburg†.

A complete description of the apparatus and of the experimental technique is to be found in the communication to which reference has been made already.

The Current Voltage Relationships occurring in an Ozonizer or Ionization Vessel.

The problem is conveniently restricted to the standardized type of vessel consisting essentially of two concentric glass or quartz tubes, the outer surface of the outer tube and the inner surface of the inner tube being arranged to serve as electrodes.

This arrangement constitutes a system of three condensers in series: the capacity C_1 of the outer wall, the capacity C_2 between the inner surface of the outer tube and the outer surface of the inner tube, and the capacity C_3 of the inner wall. It may therefore be represented in the conventional symbols as in fig. *a*, where it is assumed that for all practical purposes the power factors of C_1 and C_3 are negligibly small.

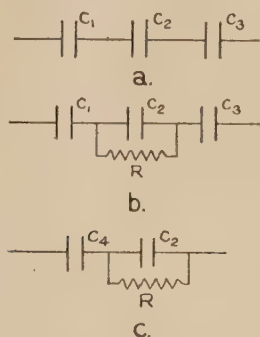
When the gas in the ozonizer is ionized, it is seen that this is equivalent, for any given value of the ionization, to a

* Communicated by Professor F. G. Donnan, F.R.S.

† Warburg, *Ann. d. Phys.* xxviii. pp. 1-17 (1909).

resistance R shunting the condenser C_2 . The system now becomes as in fig. *b*, which is itself electrically equivalent to fig. *c*, where $\frac{1}{C_4} = \frac{1}{C_1} + \frac{1}{C_3}$.

Figs. *a*, *b*, *c*.



Now let V be the total voltage applied to the system, and I the total current, and let these be out of phase by an angle ϕ .

Let $f = \frac{\omega}{2\pi}$ be the frequency, and let V_4 be the voltage across the condenser C_4 .

Then

$$I = j\omega C_4 V_4, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{where } j = \sqrt{-1}.$$

Let I_2 be the current through C_2 ,
and I_R be the current through R ,
and V be the voltage across R and C_2 .

Then

$$I_2 = j\omega C_2 V_2. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let W be the power consumed in the system in watts.

Then

$$W = VI \cos \phi.$$

Consider the vector diagram of V and I (fig. *d*).

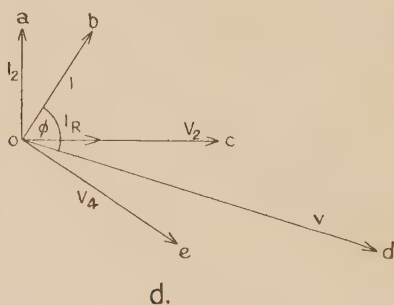
There is an associated voltage V_4 given by equation (1) in quadrature with I . Subtraction of vectors gives the voltage V_2 across the ionization space. The current in phase with V_2 and responsible for the energy generated in the system is given by

$$I_R = \frac{W}{V_2}.$$

And by subtraction of vectors the displacement current I_2 across the ionization space is obtained.

Thus having determined experimentally V , I , and W , and knowing C_1 , C_2 , and C_3 by direct measurement, it is possible to evaluate V_2 and I_R . Further, since W is constant for any given value of I , it seems reasonable to consider that the corresponding intensity of the ionization is of a constant mean value, which is attained when the rate of formation of new ions by collisions is equal to the rate of de-ionization. It follows then that R has a constant mean value, and that I_R may be identified with the current carried by the ions.

Fig. d.



This procedure is open to two objections. Firstly, that surface charges may arise on the quartz walls which will result in the potential gradient in the ionization space being different from that due to V_2 alone, and consequently the value of I_R as given by

$$I_R = \frac{W}{V_2}$$

would be in error. While it is somewhat difficult to see in what way such charges could arise in an alternating field, experiments are being devised to investigate the point, and will form the subject of another communication.

Secondly, it may be contended that the current carried by the ions may be zero except during the short intervals of time during which the potential is near its maximum value. This is equivalent to the contention that the ionization is not continuous. It has been found that the potential across the whole system V necessary to produce ionization by collision for any given gas-pressure is from three to six times greater than the maximum value of V applied when ionization has

been established. And that when the ionization, as evidenced by visual corona, has been destroyed by a momentary diminution in V , it is never possible to re-establish the ionization unless V be increased to the value initially requisite to produce ionization. It may be concluded, therefore, that the ionization and the current carried by the ions are continuous.

When the values of V are too low to be read directly, it is possible to proceed to an approximate evaluation of V_2 and I_R in the following way.

Consider the vector diagram when $\frac{I_R}{I_2} \leq 0.2$; that is, when $a\hat{o}b$ lies between $0^\circ.0$ and $11^\circ.2$.

Since $a\hat{o}b = c\hat{o}e$, we have the approximate relation

$$\begin{aligned} V &= V_2 \cos \frac{1}{2}(a\hat{o}b) + V_4 \cos \frac{1}{2}(a\hat{o}b) \\ &= 0.995V_2 + 0.995V_4; \end{aligned}$$

that is, within the experimental error in determining V ,

$$V = V_2 + V_4.$$

A first approximation to V_2 is given by

$$V_2 = \frac{I}{j\omega C_2},$$

and to I_R by

$$I_R = \frac{W}{\bar{V}_2},$$

and to I_2 by

$$I_2 = \bar{I} - \bar{I}_R.$$

A second approximation to V_2 is given by

$$V_2'' = \frac{I_2}{j\omega C_2},$$

and to I_R by

$$I_R'' = \frac{W}{\bar{V}_2''}.$$

From the values obtained for I_R , an approximate determination of the intensity of ionization can be obtained by an extension of the analysis obtaining for liquid electrolytes, which is expressed in the following way:

$$i = (U_0 + V_0)ANXe, \quad . \quad . \quad . \quad . \quad (3)$$

where i is the total current carried by the ions, A the cross-sectional area through which it flows, N the number of pairs

of ions per c.c. (in an enclosed mass of gas the number of negative and of positive ions must be identical), e the electronic charge, X the voltage gradient, and $(U_0 + V_0)$ the sum of the mobilities of the ions. As a first approximation it may be assumed that the positive ions bear a single charge, which is known to be very nearly true since the fraction of ions bearing a higher charge is extremely small*. The experimental values obtaining for the quantity X/p indicate that the negative ions are electrons†.

If U_H represents the mobility of the positive ion in hydrogen at 760 mm. and 15°C ., W the velocity of the negative ion, and p the hydrogen pressure in mms. Hg, the above equation becomes

$$i = \left(\frac{760XU_H}{p} + W \right) ANe, \quad . \quad . \quad . \quad (4)$$

since it is known that the velocity of the positive ions in hydrogen varies directly as X/p ; the value chosen for the calculations in this communication is that of Lattey and Tizard‡. W is known as a function of X/p within the range of values of this quantity obtaining in the experiments now to be described§, and the mean value has been calculated by assuming the applied voltage to be sinusoidal. The values of $i = I_R$ and of X (r.m.s.) being known from the preceding analysis, it becomes a matter of simple arithmetic to evaluate to a first approximation the mean value N of the equilibrium ionization.

EXPERIMENTAL.

Preparation of Gas.

Hydrogen, obtained from a cylinder, was scrubbed through concentrated sulphuric acid and dried by passing over 3 feet of phosphoric anhydride. It was found to contain about 0.2 per cent. of oxygen.

Ionization.

Five series of experiments were carried out with the gas at 12.5, 19.5, 26, 35, and 47 cm. at 20°C . respectively, and in each the frequency 1.5×10^7 was applied.

* J. S. Townsend, 'Electricity in Gases,' Oxford, 1915.

† Lattey & Tizard, Proc. Roy. Soc. A. lxxxvi. p. 349 (1912).

‡ Lattey & Tizard, *loc. cit.*

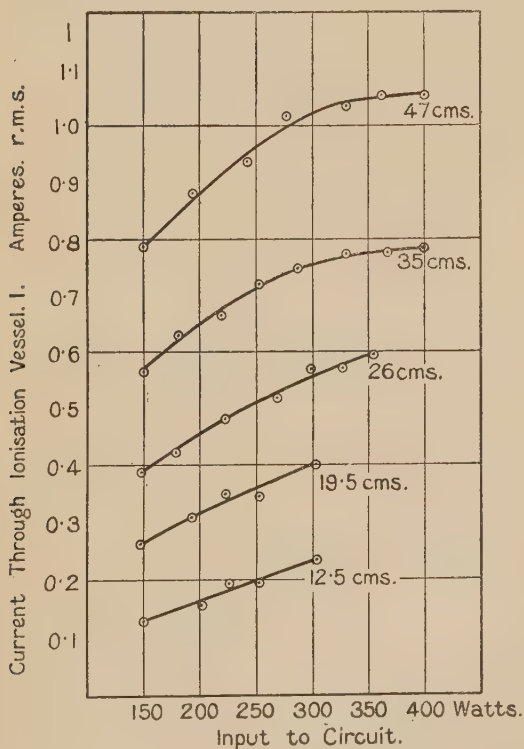
§ Lattey & Tizard, *loc. cit.* Townsend & Bailey, Phil. Mag. (6) xlii. p. 873 (1921).

At each of these pressures and for input wattages to the oscillating circuit over the range 150-400 the following quantities were determined :—

- (1) The rate of generation of heat in watts, W , in the reaction vessel.
- (2) The current, I , flowing through the ionization vessel.
- (3) The voltage, V , maintaining this current through the vessel.

The values obtained are given in figs. 1, 2, and 3 respectively.

Fig. 1.—Current flowing through Ionization Circuit.



In order to obtain strictly comparative readings, it was found essential to maintain the filament current of the valve at a constant value, which was fixed at 6.5 amperes.

Fig. 2.—Heat generated in Ionization Vessel.

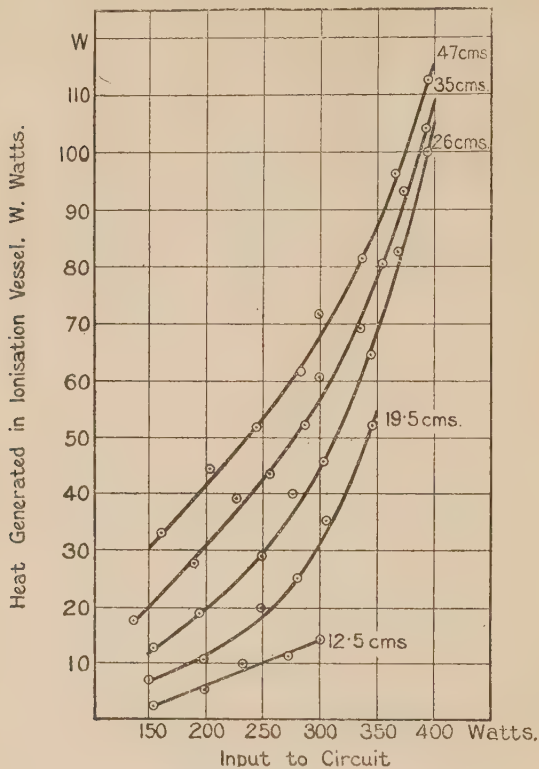
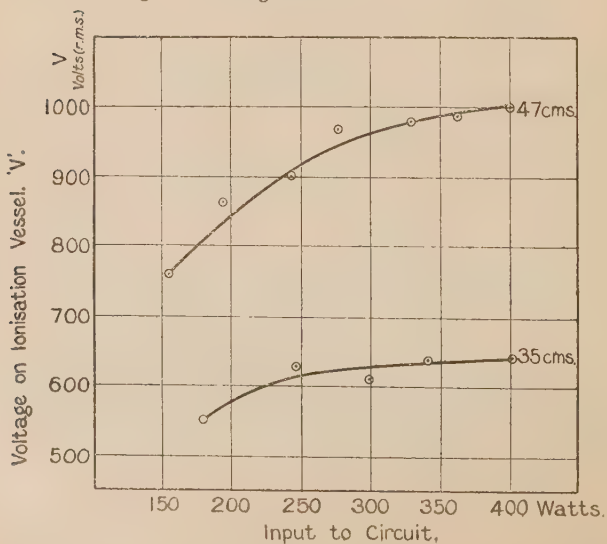


Fig. 3.—Voltage on Ionization Vessel

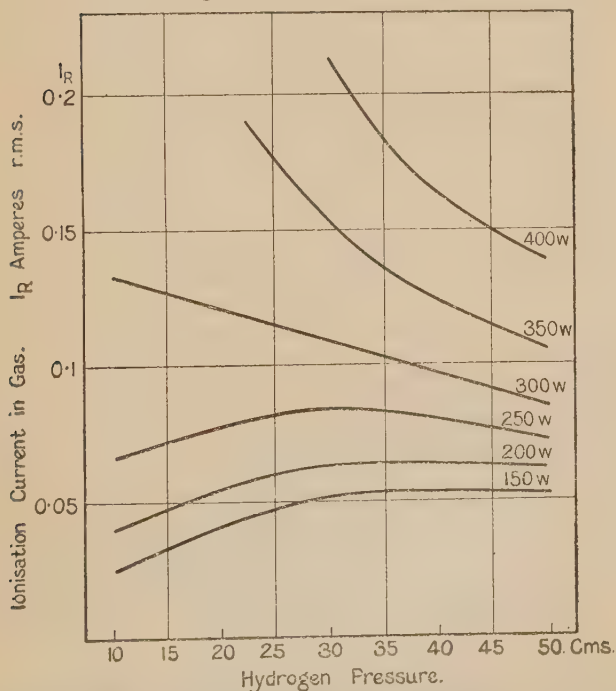


Owing to the low value of the voltage across the ionization vessel over the lower end of the pressure range, this was determined for the pressures 35 and 47 cm. only. Also due to the fact that over the lower portion of the pressure range the valve efficiency is low and the anode dissipation correspondingly high, it was impracticable to operate with input watts above about 300.

From the above values, in the manner already indicated, the corresponding values of the following quantities have been calculated :—

- (1) The ionization current I_R (fig. 4).
- (2) The ratio of the r.m.s. voltage gradient, X , in volts per cm. in the gas to the gas-pressure, p , expressed in mm. Hg at 15°C . (fig. 5).
- (3) The ratio of the mean intensity of ionization, N , to the number of molecules per c.c., N_0 , at the given pressure and at 15°C . (fig. 6).

Fig. 4.—Ionization Current.



For the sake of convenience and simplicity, the above-mentioned quantities have been expressed as functions of the hydrogen pressure over the range 10 to 50 cm. the input

1246 Dr. R. W. Lunt on the Behaviour of Hydrogen in
watts being treated as a parameter varying over the range
150 to 400 watts.

Fig. 5.—Voltage Gradient in the Ionized Hydrogen.

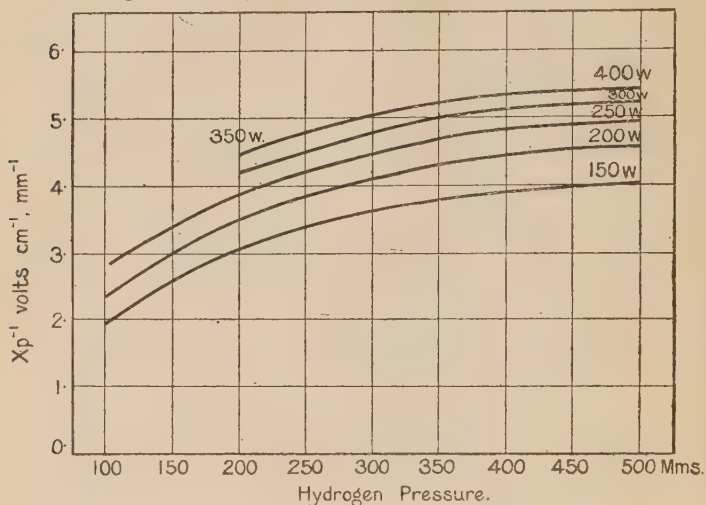
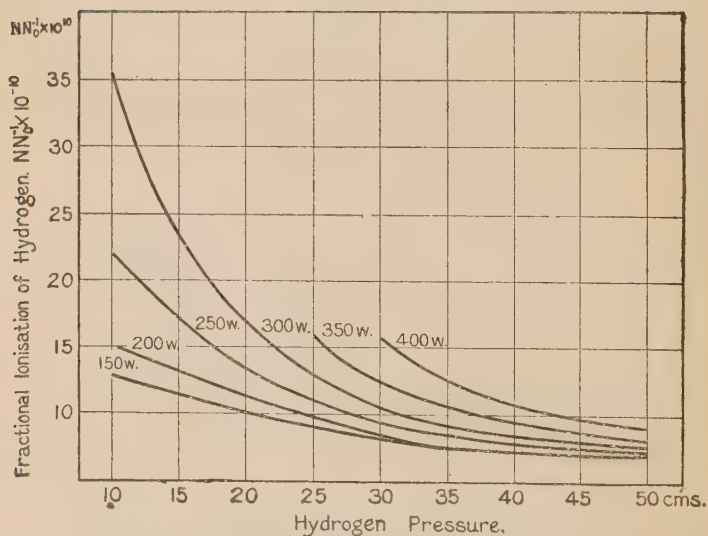


Fig. 6.—Mean Intensity of Ionization.



It is of some interest to consider the “equivalent temperature” of the ionized hydrogen—*i.e.*, that temperature at which the same density of ionization would be produced by

thermal dissociation as that observed in the ionization vessel under any given conditions.

In the following attempt to estimate the equivalent temperature, which is advanced very tentatively, it is assumed that the amount of monatomic hydrogen in existence during the discharge is negligible, and not greater than 1 or 2 per cent. of the total hydrogen. This assumption appears to be warranted by experiment. No appreciable increase in pressure has been observed when the hydrogen is ionized, except that due to a slight increase in temperature.

Consider the equations :

$$\frac{1}{2}\text{H}_2 = \text{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K_1 = \frac{p_{\text{H}}}{p_{\text{H}_2}^{\frac{1}{2}}},$$

$$F_1 = 81000 - 3.5T \log_e T + 0.00045T^2 + 1.17T *;$$

$$\text{H} = \text{H}^+ + e, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$K_2 = \frac{p_{\text{H}^+} \times p_e}{p_{\text{H}}} = \frac{p_{\text{H}^+}^2}{p_{\text{H}}},$$

$$F_2 = \frac{23070}{RT} V_i - \frac{5}{2} \log_e T - \left(\frac{5}{2} - \frac{3}{2} \log_e M_e - \frac{S_1}{R} \right) \dagger,$$

where p denotes the partial pressure of the material indicated by its suffix,

K_1 ,, the equilibrium constant of the reaction represented by equation (1),

F_1 ,, the decrease in free energy of the reaction represented by equation (1),

e ,, an electron,

H ,, a positive hydrogen ion,

K_2 ,, the equilibrium constant of the reaction represented by equation (2),

F_2 ,, the decrease in free energy of the reaction represented in equation (2),

T ,, the absolute temperature,

V_i ,, the ionization potential in volts (Hydrogen = 13.5 volts),

M_e ,, the molecular weight of an electron ;

and S_1 is given by

$$S_1 = -3.2 \text{ cal. deg.}^{-1} \dagger.$$

* Lewis & Randall, 'Thermodynamics' (New York, 1923).

† Foote & Mohler, 'Origin of Spectra' (New York, 1923).

‡ Tollman, Journ. Amer. Chem. Soc. xlii. p. 1185 (1920); xliii. p. 1592 (1921).

Then

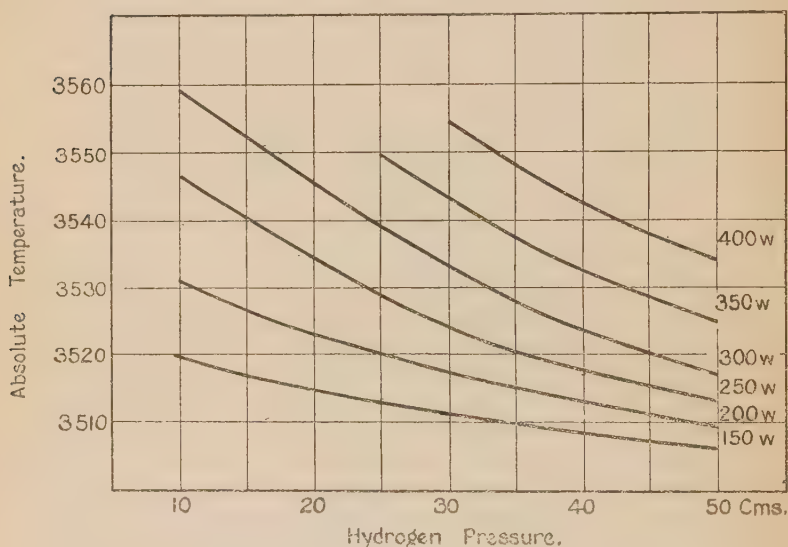
$$K_1 K_2 = \frac{p_{H^+}^2}{p_{H_2}^{\frac{1}{2}}} \quad \text{and} \quad p_{H^+} = \sqrt[4]{K_1^2 K_2^2 p_{H_2}}$$

on the above assumptions.

K_1 and K_2 having been calculated from the foregoing free energy equations, the values of $\log \frac{p_{H^+}}{p_{H_2}}$ (equilibrium values)

have been plotted against the absolute temperatures at which they are in equilibrium as abscissæ for the following values of the hydrogen pressure:— $p_{H_2} = 10, 20, 30, 40, 50$ cm.

Fig. 7.—Equivalent Temperature of Hydrogen



The quantity $\frac{p_{H^+}}{p_{H_2}}$, provided the partial pressure of monatomic hydrogen can be neglected, is identical with that represented by $\frac{N}{N_0}$. Knowing $\frac{N}{N_0}$ as a function of p_{H_2} for various input watts, the corresponding values of the "equivalent temperature" for $p_{H_2} = 10, 20, 30, 40, 50$ cm. Hg 15° C. can be read off. The resulting values are given graphically in fig. 7.

It must be observed, however, that the thermal reaction at the "equivalent temperature" would correspond to an almost complete dissociation into monatomic hydrogen.

SUMMARY.

(1) An analysis of the Siemen's Ozonizer is put forward which affords a ready determination of the voltage gradient and of the current carried by the ions in the gas.

(2) An attempt has been made to determine the approximate mean intensity of ionization in hydrogen under any given electrical conditions by a simple equation relating the conduction current in the ionized gas to the known motions of ions and electrons in hydrogen and to the impressed electric force.

(3) The two quantities, the impressed electric force and the resulting mean fractional intensity of ionization in hydrogen, have been determined at the frequency 1.5×10^7 over the pressure range 10 to 50 cm. and over the available range of electrical conditions.

(4) The concept of "equivalent temperature" is discussed with reference to the discharge in hydrogen.

In conclusion, the author wishes to express his indebtedness and thanks to the Royal Commissioners for the Exhibition of 1851 for a Scholarship, and to the Trustees of the Ramsay Memorial Fellowship Trust for a Fellowship, which have enabled the above work to be carried out; to Messrs. The Marconi Wireless Telegraph Company, and to Mr. E. Green, M.Sc., of that Company; to Messrs. Brunner, Mond & Company, for the loan of apparatus; to his friend Mr. F. D. Smith, M.Sc., to whom he owes the vector solution of the Siemen's Ozonizer; to Professor C. L. Fortescue, of the City & Guilds' Engineering College, South Kensington; and especially to Professor F. G. Donnan, F.R.S., at whose suggestion the work was undertaken, for his deep interest and suggestive advice during the progress of the research.

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Physical Chemistry Laboratories,
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CXXVI. *A Note on Musical Atmospheric Disturbances.* By
T. L. ECKERSLEY, M.A., *Research Department, Marconi's
Wireless Telegraphy Co.* *.

IT has been known to workers in "Radio" for some years that if a telephone or any other audio-recorder system is placed directly in series with a large aerial, disturbances of a musical nature can be heard.

These have a very peculiar character: the pitch of the note invariably starts above audibility, often with a click, and then rapidly decreases, finally ending up with a low note of more or less constant frequency which may be of the order of 300 to 1000 a second.

The duration of the complete disturbances varies very considerably; at times it may be a very small fraction of a second, and at others it may be even $1/5$ of a second.

Some workers have noticed a regular diurnal variation in the character and frequency of these disturbances. In the early morning disturbances of this type are very infrequent and the duration is short. The frequency and duration increase as the day advances, and may be very considerable towards the late afternoon and evening. They are greatest during the night.

These disturbances are obviously of an external origin, and do not owe their character to the resonance of the receiver system under "shock excitation." The explanation offered here is based on Dr. Eccles' theory of ionic refraction, and may be able to yield data of considerable importance relating to the physical constants of the "upper conducting layer," which plays such an important part in radio transmission.

Briefly, the occurrence of these disturbances is attributed to the dispersion of an electrical impulse in a medium loaded with ions.

For, as Dr. Eccles has shown, the presence of free ions has the effect of apparently decreasing the specific inductive capacity of the medium by an amount depending on the frequency of the waves travelling through it.

The loading effected by the free ions gives the medium a dispersive character, since the transmission constants vary with the frequency of the impressed waves. Under these conditions we have, as is well known, to distinguish between the "Group velocity" and the "Phase velocity" of an individual wave in the group.

* Communicated by Prof. S. Chapman, F.R.S.

It is not difficult to calculate these. We can take as a basis the ordinary electromagnetic equations, and no loss of generality will be occasioned by the choice of a simple plane wave, since the solutions are linear (when we neglect the effect of the magnetic field in the wave front) and any system of wave motion can be built up out of these waves.

We will take, therefore,

$$\text{curl } \mathbf{E} = -\frac{\mu}{c} \frac{\partial \mathbf{H}}{\partial t}, \quad \text{curl } \mathbf{H} = \mathbf{K} \frac{\partial \mathbf{E}}{\partial t} + v\rho,$$

where ρ is the electrical density of the ions and v their velocity

$$\mathbf{E} = X, Y, Z, \quad \mathbf{H} = \alpha, \beta, \gamma.$$

Assume a plane wave propagated in the x direction, β and Z only existing; then

$$\frac{\partial Z}{\partial x} = -\mu \frac{\partial \beta}{\partial t},$$

$$\frac{\partial \beta}{\partial x} = \mathbf{K} \frac{\partial Z}{\partial t} + vNe,$$

$$\text{or} \quad \frac{\partial^2 Z}{\partial x^2} = \frac{\mu \mathbf{K}}{c^2} \frac{\partial^2 Z}{\partial t^2} + \frac{\partial}{\partial t} Nev, \quad . \quad . \quad . \quad . \quad (1)$$

and the equation for v is given by

$$m \frac{\partial v}{\partial t} + fv = Ze;$$

if we neglect effects due to collisions, then fv can be neglected in comparison with $m \frac{\partial v}{\partial t}$.

If the waves are periodic, p being $2\pi \times$ frequency, the last equation may be put

$$impv = Ze$$

(neglecting the term fv); on substituting for v in (1) we get V^2 the square of the phase velocity:

$$V^2 = c^2 \frac{1}{\left(1 - \frac{Ne^2e}{m\mu^2}\right)}, \text{ where } \mu\mathbf{K}=1,$$

$$\text{or} \quad V = c \sqrt{1 + \frac{\lambda^2}{\lambda_1^2}}, \text{ where } \lambda_1^2 = \frac{4\pi^2 mc^2}{Ne^2},$$

$$\text{or} \quad V = c \sqrt{1 + \frac{\kappa_1^2}{\kappa^2}}, \text{ where } \kappa = 2\pi/\lambda.$$

The group velocity

$$= \frac{\partial \kappa V}{\partial \kappa} = U = \frac{c}{\sqrt{1 + \kappa_1^2 / \kappa^2}},$$

and

$$UV = c^2.$$

We can use an approximate method, due to Prof. Havelock, to determine the subsequent history of a sudden impulse or what he called a "limited initial disturbance." But it is possible, without the aid of an elaborate mathematical analysis, to obtain an idea of this.

Any impulse can be split up by the aid of Fourier's analysis into a "band of spectrum of all frequencies";

for an example, an impulse of the form $\frac{a^2}{a^2 + t^2}$ is expressible as $\frac{1}{\pi} \int_0^\infty e^{-ap} \sin pt \, dp$, which shows that for all frequencies

which are small compared with $1/a$ the intensity in the spectrum is nearly constant. In a linear dispersive medium each component of the "spectrum" is transmitted with its appropriate velocity, and the result will be that after a suitable interval, long or short according to the amount of "dispersion" in the medium, the various frequencies will be all separated out. Thus waves of length λ will be found after a time t in the neighbourhood of the distance tU_λ , where U_λ is the appropriate *group* velocity for this wave-length.

The group velocity is involved here, and not the phase velocity, because elementary analysis shows that a group of waves of the wave-length λ moves as a whole with the velocity U_λ , although the individual waves in the group move with the velocity V_λ , *i.e.* are continually moving through the group.

Now U_λ is small for large values of λ and increases as λ is decreased up to the limiting value c , the velocity of light, when $\lambda \rightarrow 0$. The short wave-lengths travel fastest and arrive first, and the long wave-lengths last.

To a stationary observer this appears as a note of rapidly decreasing frequency and bears a strong resemblance to the actual sounds heard.

It must be left to actual measurements and theoretical calculation to decide how close this resemblance is.

It is shown (Cambridge Tracts in Mathematics and Mathematical Physics, No. 17) by Prof. Havelock that the subsequent history of a limited initial disturbance can

be calculated with a fair degree of accuracy from the formula :

$$y = \frac{1}{2\pi} \left\{ \frac{2\pi}{t \left(\frac{\partial U}{\partial \kappa} \right)_0} \right\}^{1/2} \cos \{k_0(x - V_0 t) \pm \pi/4\}, \quad (2)$$

where k_0 is expressed in terms of x and t by the formula

$$x - U_0 t = 0, \quad (3)$$

where U_0 in this case is

$$U_0 = \frac{c}{\sqrt{1 + \frac{\kappa_1^2}{\kappa^2}}}, \quad \left(\frac{\partial U_0}{\partial \kappa} \right) = \frac{c}{\kappa^2} \frac{\kappa_1^2}{\kappa} \frac{1}{(1 + \kappa_1^2/\kappa^2)^{3/2}}.$$

Expressing these quantities in terms of x and t by relation (3) we get the following expression for y :

$$y = \frac{1}{2\pi} \left\{ \frac{2\pi\kappa_1}{ct \left\{ 1 - \frac{x^2}{c^2 t^2} \right\}^{3/2}} \right\}^{1/2} \cos \{ \kappa_1 (x^2 - c^2 t^2)^{1/2} + \pi/4 \}.$$

This expression represents a disturbance of varying frequency, the high frequency starting first and tailing down to a low frequency as time elapses.

Limiting Frequency.

When ct is large compared with x , *i. e.* if we consider the tail-end of the disturbance, we get approximately

$$y = \frac{1}{2\pi} \left\{ \frac{2\pi\kappa_1}{ct} \right\}^{1/2} \cos (\kappa_1 ct),$$

which represents a disturbance of constant frequency $\frac{\kappa_1 c}{2\pi}$, and of gradually decreasing amplitude.

This constant limiting frequency is another point of resemblance with actual fact, and the equation

$$n_1 = \frac{\kappa_1 c}{2\pi} = \frac{1}{2\pi} \left(\frac{e^2 N}{m} \right)^{1/2}$$

gives values of N , the number of ions per c.c., for different types of ions.

If we assume for instance that the ions are electrons, and it will be seen that they contribute chiefly to the value of Ne , we get

$$n = \frac{1}{2\pi} (1.7 \times 10^7) (eN)^{1/2};$$

so that if $n=300$ we get eN of the order 2.2×10^{-21} , which is of the order of 1 ion per c.c.

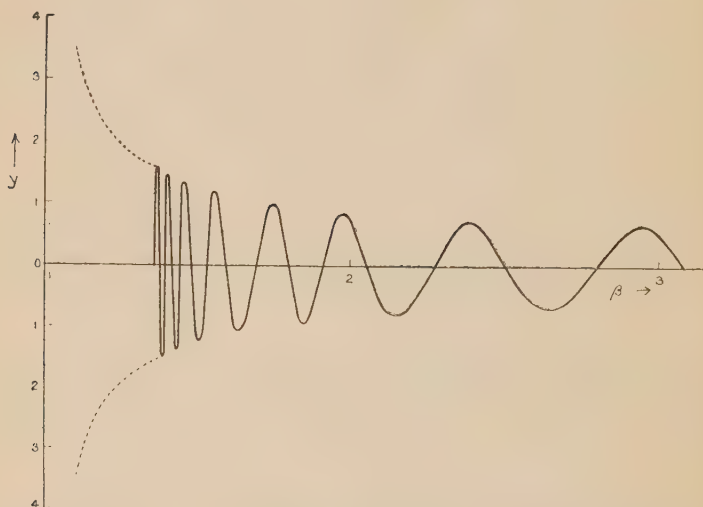
The attached curve, fig. 1, shows y as a function of $ct/x = \beta$ with $\kappa_1 v = 3\pi$ approx., *i. e.* at a distance where the component frequencies have been well separated out.

Fig. 1.

Form of Disturbance computed from the Formula

$$y = \frac{1}{2\pi} \left\{ \frac{\frac{\kappa_1}{x}}{\beta \left(1 - \frac{1}{\beta^2}\right)^{3/2}} \right\}^{1/2} \cos \left\{ \kappa_1 x (1 - \beta^2)^{1/2} + \pi/4 \right\}.$$

$$\beta = \frac{ct}{x}, \quad \kappa_1 x = 3\pi \text{ approx.}$$



The part in the neighbourhood of $x = ct$, *i. e.* the head of the disturbance, is probably inaccurate and anyhow depends on the shape and thickness of the original impulse. It is therefore shown dotted, and only the envelope of the waves given.

An attempt to get a more accurate representation than the one given by the approximate formula (fig. 1) is developed here, and it will be found that when ct is large compared with x the original formula is approximately correct.

If V is the phase velocity corresponding to the wavelength λ and $\kappa = \frac{2\pi}{\lambda}$, then we can express the subsequent history of a pulse $\frac{a^2}{a^2 + x^2}$ in the form

$$y = \text{a real part of } \frac{1}{\pi} \int_0^\infty e^{-a\kappa + i\kappa(x - Vt)} d\kappa, \quad . \quad . \quad (4)$$

where V is expressible in terms of κ in the form

$$V = c \sqrt{1 + \kappa_1^2 / \kappa^2}$$

so that $\kappa V = c^2 \sqrt{\kappa^2 + \kappa_1^2}$;

we have therefore to evaluate the integral

$$y = \frac{1}{\pi} \int_0^\infty d\kappa e^{i\kappa(x+ia) - i \sqrt{\kappa^2 + \kappa_1^2} ct}, \quad . \quad . \quad (5)$$

or

$$\frac{1}{\pi} \int_0^\infty d\kappa e^{i\kappa x_1 - i \sqrt{\kappa^2 + \kappa_1^2} ct},$$

where $x_1 = x + ia$.

Let $U = \kappa/\kappa_1$ and $U = \sinh v$,

then $y = \frac{\kappa_1}{\pi} \int_0^\infty e^{i\kappa_1 x_1 \sinh v - i\kappa_1 ct \cosh v} \cosh v dv$.

Now let

$$\begin{aligned} ct &= R \cosh \phi, & R^2 &= (c^2 t^2 - x_1^2), & . \quad . \quad (6) \\ x_1 &= R \sinh \phi, \end{aligned}$$

$$i\kappa_1(x_1 \sinh v - ct \cosh v) = -iR\kappa_1 \cosh (v - \phi);$$

so that if $w = v - \phi$

$$\begin{aligned} y &= \frac{\kappa_1}{\pi} \int_{-\phi}^{+\infty} e^{-i\kappa_1 R \cosh w} \cosh (w + \phi) dw \\ &= \frac{\kappa_1}{\pi} \int_{-\phi}^{\infty} \cosh \phi e^{-i\kappa_1 R \cosh w} \cosh w dw \\ &\quad + \frac{\kappa_1}{\pi} \int_{-\phi}^{+\infty} \sinh \phi e^{-i\kappa_1 R \cosh w} \sinh w dw. \end{aligned}$$

The latter term can be integrated immediately ; it is

$$\frac{\sinh \phi}{\pi R} \cdot e^{i\kappa_1 R \cosh \phi},$$

and taking (6) into account this becomes

$$\frac{1}{\pi} \frac{x_1}{c^2 t^2 - x_1^2} e^{i\kappa_1 ct}.$$

It should be observed that the *Real Part of* $-iR$ is *Negative*.

The other term,

$$\begin{aligned} &\frac{\kappa_1}{\pi} \int_{-\phi}^{\infty} \cosh \phi e^{-i\kappa_1 R \cosh w} \cosh w dw \\ &= \frac{\kappa_1}{\pi} \int_{-\phi}^0 \cosh \phi e^{-i\kappa_1 R \cosh w} \cosh w dw \\ &\quad + \frac{\kappa_1}{\pi} \int_0^{\infty} \cosh \phi e^{-i\kappa_1 R \cosh w} \cosh w dw, \end{aligned}$$

This latter term is $\frac{\kappa_1}{\pi} \cos \phi K_1(i\kappa_1 R)$ where $K_1(x)$ is the second Bessel Function of order 1 when the real part of $-i\kappa_1 R$ is negative; and if ϕ is small, i. e. $ct \gg x$, the first term is nearly zero.

The total is therefore

$$\frac{1}{2\pi} \sqrt{\frac{2\pi\kappa_1}{ct\left(1-\frac{x^2}{c^2t^2}\right)^{3/2}}} \cos \{\kappa_1(x_1^2 - c^2t^2)^{1/2}\} \\ + \frac{1}{\pi} \frac{x_1}{(c^2t^2 - x_1^2)} \cos \kappa_1 ct + \frac{\kappa_1}{\pi} \int_{-\phi}^0 \cosh \phi e^{-i\kappa_1 R \cosh w} \cosh w dw,$$

on replacing $K_1(i\kappa_1 R)$ by its asymptotic value. This reduces to the former value (2) when ct is large compared with x .

When x is approximately equal to ct , ϕ is always a finite quantity when " a " is finite, for

$$\cosh \phi = \frac{ct}{\sqrt{2aix}} \text{ approx. if } \phi = p + iq;$$

then

$$\tanh p = 1 - \frac{2ax}{ax + c^2t^2} \text{ approx. and } p \rightarrow \infty, \quad a \rightarrow 0,$$

$$\tan q = 1 + \frac{2ax}{ax + c^2t^2} \quad ,, \quad q \rightarrow \frac{\pi}{4}, \quad ,,$$

If we integrate from $-iq - p$ to $-p$ and from $-p$ to 0 when a is small, the latter part, i. e. \int_{-p}^0 , becomes very nearly

$$\kappa_1 \frac{\cosh \phi}{\pi} K_1(i\kappa_1 R),$$

and the former part is negligible except in the neighbourhood of $w = -\phi$, and tends to zero when ct is large.

The total when ct and x are large and nearly equal is

$$\frac{2\kappa_1 \cosh \phi}{\pi} (K_1(i\kappa_1 R)) + \frac{1}{\pi} \frac{x_1}{c^2t - x_1} \cos \kappa_1 ct.$$

This shows that the approximate form is only accurate when ct is large compared with x , but the conclusion that a limiting frequency $\frac{\kappa_1 c}{2\pi}$ is reached is shown to be accurately true. A measurement of this frequency should therefore be of value in determining the constants of the conductive medium.

The fact that these peculiar types of disturbance occur

almost entirely at night suggest that they have their origin in the permanent auroral conducting layer, and not in the lower layer ionized in the daytime. The value of N_e should therefore apply to this low-pressure region, and not to the relatively high-pressure zone where the attenuation of radio waves is so high as to eliminate all types of disturbance originating above it.

As we have seen, the approximate values of N_e for electrons are of the order 2×10^{-21} to 2×10^{-22} , and for α -particles 2.7×10^{-18} to 2.7×10^{-19} . This is of the order of one electrified particle per c.c. It is very difficult to say in what region of the auroral layer these impulses originate. If we assume the outside, the waves have to pass right through the medium and the value of N_e is probably an average of the quantity throughout the layer.

If, on the other hand, we assume that the impulses are produced by the sudden stoppage of groups of particles at the bottom edge of the layer, the value of N_e should be that corresponding to the lower fringe of the layer.

If the conductivity is known, as well as N_e , we can estimate T , the mean free life of an electron in the region where the impulses originate. For the conductivity σ is $N_e \cdot \frac{e}{m} T$, and when N_e , $\frac{e}{m}$, and σ are known, T can be

deduced. The average conductivity has been estimated by Schuster (in his theory of the diurnal variations of the earth's magnetism) to be of the order 10^{-14} c.g.s. units if the layer is assumed to be 300 km. thick. S. Chapman has estimated that the total conduction is equivalent to a layer of copper 1 metre thick, but the magnetic evidence is insufficient to give the actual conductivity at any point in the layer. The evidence afforded by the attenuation of radio waves at night is the most relevant. Unfortunately, the attenuation constant does not determine an unique value of the conductivity; two values are possible, *i.e.* approx.

$\frac{1}{1.7} \times 10^{-14}$ and $\frac{1}{3} \times 10^{-19}$. These values refer to the effective conductivities for high frequencies (n in the neighbourhood of 10^4), which are derived from the steady current conductivities according to the relation

$$\sigma = \sigma_0 / \sqrt{1 + \left(\frac{2\pi T}{t}\right)^2} \quad \text{or} \quad \sigma = \frac{Ne^2 T}{m} / \sqrt{1 + \left(\frac{2\pi T}{t}\right)^2},$$

where t is the time period of the electromagnetic waves and T has the same significance as before.

Equating this to $4 \cdot 10^{-19}$, Ne to 2×10^{-22} , and t to $10^{-4}e/m = 1 \cdot 77 \times 10^7$, we have

$$\frac{2\pi T}{t} \bigg/ \sqrt{1 + \left(\frac{2\pi T}{t}\right)^2} = \frac{10^{-19} \times 2\pi \times 10^7}{3 \times 1 \cdot 77 \times 10^7 \times 2 \times 10^{-22}},$$

or

$$\left(\frac{2\pi T}{t}\right)^2 \bigg/ 1 + \left(\frac{2\pi T}{t}\right)^2 = 0 \cdot 35;$$

$$i. e. \quad \frac{2\pi T}{t} = 0 \cdot 89,$$

$$T = \frac{1}{70,500} \text{ approx.}$$

If, on the other hand, we use the other possible value of σ , *i. e.* $\frac{1}{1 \cdot 7} \times 10^{-14}$, the equation $Ne \frac{e}{m} T \bigg/ \sqrt{1 + \left(\frac{2\pi T}{t}\right)^2} = \sigma$ cannot be satisfied by any real value of T ; for we get, when $x = \left(\frac{2\pi T}{t}\right)$,

$$\frac{x}{\sqrt{1+x^2}} = \frac{10^{-14} \times 2\pi \times 10^4}{1 \cdot 7 \times 1 \cdot 77 \times 10^7 \times 2 \times 10^{-22}} = \frac{\pi \times 10^6}{1 \cdot 7 \times 1 \cdot 77} \gg 1$$

and the relation cannot be satisfied by any real value of T . The calculation therefore suggests that ρ is of the order 3×10^{19} and $T = \frac{1}{70,000}$ if we assume that the impulses, which give rise to the musical strays, originate in the lower fringe of the conducting layer which is responsible for the attenuation of radio waves at night.

In confirmation of this we have further evidence derived from this source. With resistivities as high as this, the attenuation takes the form $e^{-\frac{2\pi}{\rho n} x}$, where ρ_n is the resistivity at the frequency n . Now $f_n = \rho_0 \sqrt{1 + \left(\frac{2\pi T}{t}\right)^2}$, where ρ_0 is the resistivity for sufficiently low frequencies, and T and t have the same significance as before. The attenuation constant should therefore be of the form :

$$\frac{A}{\sqrt{1+p^2/p_0^2}}, \text{ where } p = 2\pi n, \quad p_0 = \frac{1}{T}.$$

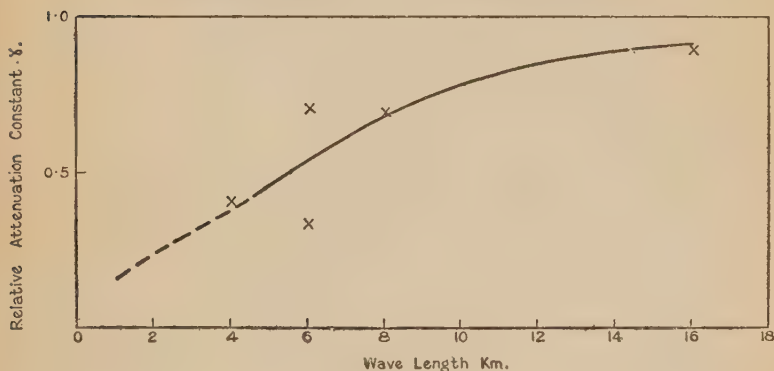
The curve (fig. 2), derived from approximate data, shows that this is roughly the case. Calculating T from the

curve we get $T = \frac{1}{100,000}$, which does not differ greatly from the previous value. The analytical expression (fig. 2) takes no account of the attenuation which must occur in the dispersive medium by the intercollision of the free electrons and ions.

I hope in a later paper to show that the attenuation introduced by this dissipation does not materially influence the results obtained here. The approximate results indicate that the tail-end of the disturbance is most attenuated, but the fact that the limiting frequency is approached fairly closely in practice shows that this attenuation cannot be excessive.

Fig. 2.

Approximate Relative Values of Night Attenuation.



This result should lead to an independent estimate of T , which should act as a check on the theory.

Recently Sir Joseph Larmor has developed a theory of radio transmission in which the observed bending of the rays round the earth is attributed to the same mechanism as is assumed in this paper, and the results he arrives at are in substantial agreement with those obtained here.

In particular he arrives at the result that N , the number of electrons per c.c., need not exceed 1, which is in good agreement with the results obtained here.

Again, the value $T = 10^{-5}$ is in agreement with Larmor's value.

For the value T_0 between actual encounters is estimated by him to be $\frac{1}{30} 10^{-5}$, but from the mode of origin of T this quantity is obviously the time between encounters

which involve a large dissipation of energy, and, as he has pointed out, laboratory experience has shown that an electron can pass through an atom with but slight derangement of its motion in all but exceptional cases, implying that T is large compared with T_0 and may well be 30 times as great.

This factor would bring the two determinations of T into agreement.

CXXVII. *Determination of the Minimum Plane in Four-Dimensional Space with respect to a System of Non-Coplanar Points.* By H. S. UHLER, B.A., Ph.D., Associate Professor of Physics, Yale University*.

Synopsis.—The material presented after the introductory remarks will comprise in order the following items: (a) derivation of a general formula for the length of the perpendicular dropped from a point to a plane in four-space; (b) use of this distance formula in the Method of Least Squares; (c) proof of the significant fact that the complete sextic equation which arises in part (b) can always be reduced to a cubic; and (d) evaluation of a numerical illustration.

Introduction.—The primary object of this paper is to derive a set of exact formulas for the determination of the position of a plane in four-dimensional space, such that the sum of the squares of the lengths of the perpendiculars dropped from any (large enough) number of given points upon the plane shall be a minimum. In non-geometrical language, the problem may be interpreted as that of the determination of the most probable values of the coefficients in two appropriate linear equations involving four variables with respect to the observational data of a given system which does not satisfy any pair of linear equations. The error curve is assumed to be the normal distribution of Gauss, and the variables are treated as having equal mathematical weights. The condition stated last does not limit the generality of the solution, since for unequal weights it is always possible to transform the coordinates to a new set of variables having equal weights, to solve the transformed problem, and finally to return to the original set †.

* Communicated by Prof. W. F. G. Swann.

† H. S. Uhler, "Method of Least Squares and Curve Fitting," *Journ. Opt. Soc. Amer. and Rev. Sci. Instrs.*, vol. vii. no. 11, p. 1043 (1923).

THE present paper supplements one written by Karl Pearson entitled "On Lines and Planes of Closest Fit to Systems of Points in Space" [this Magazine, 6th series, vol. ii. pp. 559-572 (1901)]. By the term "plane" Pearson means a linear space having $n-1$ degrees of freedom in n -dimensional flat space. Hence, for $n=4$ he has solved the cases of the hyperplane (3-space) and the straight line. Both papers contain material which may be useful in the theory of correlation. Pearson's "standard-deviations" $\sigma_w, \sigma_x, \sigma_y, \sigma_z$, and the σ 's first introduced below in equation (19) may be converted into one another by the relations

$$\sigma_w = \frac{\sqrt{\sigma_{11}}}{\kappa}, \quad \sigma_x = \frac{\sqrt{\sigma_{22}}}{\kappa}, \quad \sigma_y = \frac{\sqrt{\sigma_{33}}}{\kappa}, \quad \sigma_z = \frac{\sqrt{\sigma_{44}}}{\kappa}.$$

Similarly his "correlation coefficients" or r 's may be calculated from the σ 's of the present article by means of the generally irrational equations

$$r_{wx} = \frac{\sigma_{12}}{\sqrt{\sigma_{11}\sigma_{22}}}, \quad r_{wy} = \frac{\sigma_{13}}{\sqrt{\sigma_{11}\sigma_{33}}}, \quad \dots, \quad r_{yz} = \frac{\sigma_{34}}{\sqrt{\sigma_{33}\sigma_{44}}}.$$

(a) Let the non-homogeneous equations of the hyperplanes which intersect in the plane and determine it be

$$\left. \begin{aligned} \alpha w + \beta x + \gamma y + \delta z + \epsilon &= 0, \\ \alpha' w + \beta' x + \gamma' y + \delta' z + \epsilon' &= 0, \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where w, x, y , and z are the rectangular coordinates of any point in the plane. Let M denote the array or matrix

$$\begin{array}{cccc} \alpha & \beta & \gamma & \delta \\ \alpha' & \beta' & \gamma' & \delta', \end{array}$$

the rank of which will be assumed to be two. Let Δ symbolize the distance between the point (w', x', y', z') which does not lie in the plane represented by equations (1) and the point (w, x, y, z) . Then

$$(w-w')^2 + (x-x')^2 + (y-y')^2 + (z-z')^2 - \Delta^2 = 0. \quad (2)$$

The coordinates w, x, y , and z are to be varied in such a manner as to make Δ a minimum subject to the conditions imposed by equations (1). In Euclidean space this process will adjust the straight line joining the points (w, x, y, z) and (w', x', y', z') to perpendicularity to the plane. Hence

differentiate equations (2) and (1), and put $d\Delta=0$ to obtain

$$\left. \begin{aligned} (w-w')dw + (x-x')dx + (y-y')dy + (z-z')dz &= 0, \\ \alpha dw + \beta dx + \gamma dy + \delta dz &= 0, \\ \alpha' dw + \beta' dx + \gamma' dy + \delta' dz &= 0. \end{aligned} \right\} \quad (3)$$

Following Lagrange's method of undetermined factors, multiply the first, the second, and the third equation of set (3) respectively by m , $-\mu$, $-\mu'$, then add, and equate to zero the resulting polynomial coefficients of the differentials dw , dx , dy , and dz to get

$$\left. \begin{aligned} (w-w')m - \alpha\mu - \alpha'\mu' &= 0, \\ (x-x')m - \beta\mu - \beta'\mu' &= 0, \\ (y-y')m - \gamma\mu - \gamma'\mu' &= 0, \\ (z-z')m - \delta\mu - \delta'\mu' &= 0. \end{aligned} \right\} \quad \dots \quad (4)$$

Let F and F' denote the values obtained by substituting in equations (1) the fixed coordinates of the point (w', x', y', z') for those of the variable point (w, x, y, z) ; that is

$$\begin{aligned} F &\equiv \alpha w' + \beta x' + \gamma y' + \delta z' + \epsilon \\ \text{and} \quad F' &\equiv \alpha' w' + \beta' x' + \gamma' y' + \delta' z' + \epsilon'. \end{aligned}$$

Now multiply the first equation of set (1), and the successive equations of set (4) read downward by m , $-\alpha$, $-\beta$, $-\gamma$, $-\delta$ respectively, and add the products thus formed to find the second equation of set (5) below. In like manner multiply the second equation of set (1) and equations (4) in order by m , $-\alpha'$, $-\beta'$, $-\gamma'$, $-\delta'$, and add the results to get the third equation of group (5). The first equation of this group is the sum of the products obtained by multiplying equation (2) and equations (4) respectively by $-m$, $w-w'$, $x-x'$, $y-y'$, and $z-z'$.

$$\left. \begin{aligned} \Delta^2 m + F\mu + F'\mu' &= 0, \\ Fm + (\alpha^2 + \beta^2 + \gamma^2 + \delta^2)\mu + (\alpha\alpha' + \beta\beta' + \gamma\gamma' + \delta\delta')\mu' &= 0, \\ F'm + (\alpha'\alpha + \beta'\beta + \gamma'\gamma + \delta'\delta)\mu + (\alpha'^2 + \beta'^2 + \gamma'^2 + \delta'^2)\mu' &= 0, \\ &\dots \end{aligned} \right\} \quad (5)$$

A necessary and sufficient condition that equations (5) may have a solution other than $m=\mu=\mu'=0$ is

$$\begin{vmatrix} \Delta_0^2, & F, & F' \\ F, & \alpha^2 + \beta^2 + \gamma^2 + \delta^2, & \alpha\alpha' + \beta\beta' + \gamma\gamma' + \delta\delta' \\ F', & \alpha'\alpha + \beta'\beta + \gamma'\gamma + \delta'\delta, & \alpha'^2 + \beta'^2 + \gamma'^2 + \delta'^2 \end{vmatrix} = 0, \quad (6)$$

where the subscript zero emphasizes the fact that the value of Δ derived from the solution of equation (6) is a minimum.

For the present purposes it is necessary to expand the above bordered symmetrical determinant. This may be accomplished in the following manner. Let this determinant be written as $D\Delta_0^2 - N$. By compounding M with its conjugate

$$\begin{array}{c} \alpha \quad \alpha' \\ \beta \quad \beta' \\ \gamma \quad \gamma' \\ \delta \quad \delta' \end{array}$$

it is seen at once that

$$D = (\alpha\beta' - \alpha'\beta)^2 + (\alpha\gamma' - \alpha'\gamma)^2 + (\alpha\delta' - \alpha'\delta)^2 \left. \begin{array}{l} + (\beta\gamma' - \beta'\gamma)^2 + (\beta\delta' - \beta'\delta)^2 + (\gamma\delta' - \gamma'\delta)^2 \end{array} \right\} \quad (7)$$

By applying Cauchy's theorem* for the expansion of a bordered determinant D as a homogeneous function of the bordering constituents it is readily found that

$$N = (\alpha F' - \alpha' F)^2 + (\beta F' - \beta' F)^2 + (\gamma F' - \gamma' F)^2 + (\delta F' - \delta' F)^2. \quad (8)$$

Let

$$\begin{array}{ll} l \equiv (\alpha\beta' - \alpha'\beta) / \sqrt{D}, & p \equiv (\beta\gamma' - \beta'\gamma) / \sqrt{D}, \\ m \equiv (\alpha\gamma' - \alpha'\gamma) / \sqrt{D}, & q \equiv (\beta\delta' - \beta'\delta) / \sqrt{D}, \\ n \equiv (\alpha\delta' - \alpha'\delta) / \sqrt{D}, & r \equiv (\gamma\delta' - \gamma'\delta) / \sqrt{D}. \end{array}$$

Then equation (7) becomes

$$l^2 + m^2 + n^2 + p^2 + q^2 + r^2 = 1, \quad (9)$$

and the identity

$$\begin{aligned} & (\alpha\beta' - \alpha'\beta)(\gamma\delta' - \gamma'\delta) - (\alpha\gamma' - \alpha'\gamma)(\beta\delta' - \beta'\delta) \\ & + (\alpha\delta' - \alpha'\delta)(\beta\gamma' - \beta'\gamma) = 0 \end{aligned}$$

changes to

$$lr - mq + np = 0. \quad (10)$$

Substitution in equation (8) of the expressions for F and F' given just after equations (4) leads to

$$\begin{aligned} \Delta_0^2 = N/D = & [lx' + my' + nz' + (\alpha\epsilon' - \alpha'\epsilon) / \sqrt{D}]^2 + [py' + qz' - lw' \\ & + (\beta\epsilon' - \beta'\epsilon) / \sqrt{D}]^2 + [rz' - mw' - px' + (\gamma\epsilon' - \gamma'\epsilon) / \sqrt{D}]^2 \\ & + [-nw' - qx' - ry' + (\delta\epsilon' - \delta'\epsilon) / \sqrt{D}]^2. \quad (11) \end{aligned}$$

Expression (11) may be changed to the form best adapted to the main problem by letting the given point

* R. F. Scott & G. B. Mathews, 'Theory of Determinants,' p. 47, § 25.

$(\bar{w}, \bar{x}, \bar{y}, \bar{z})$ lie in the plane. Then

$$\begin{aligned}(\alpha\epsilon' - \alpha'\epsilon) / \sqrt{D} &= -l\bar{x} - m\bar{y} - n\bar{z}, \\(\beta\epsilon' - \beta'\epsilon) / \sqrt{D} &= -p\bar{y} - q\bar{z} + l\bar{w}, \\(\gamma\epsilon' - \gamma'\epsilon) / \sqrt{D} &= -r\bar{z} + m\bar{w} + p\bar{x}, \\(\delta\epsilon' - \delta'\epsilon) / \sqrt{D} &= n\bar{w} + q\bar{x} + r\bar{y}.\end{aligned}$$

$$\Delta_0^2 = (nW' + qX' + rY')^2 + (lX' + mY' + nZ')^2 + (pY' + qZ' - lW')^2 + (-rZ' + mW' + pX')^2, \quad (12)$$

where

$$W' \equiv \bar{w} - w', \quad X' \equiv \bar{x} - x', \quad Y' \equiv \bar{y} - y', \quad Z' \equiv \bar{z} - z'.$$

Formula (12) gives directly the square of the length of the perpendicular dropped from the point (w', x', y', z') to the plane represented by any two of the equations of set (13).

$$\left. \begin{aligned}E_1 &\equiv l\bar{x} + m\bar{y} + n\bar{z} - (l\bar{x} + m\bar{y} + n\bar{z}) = 0, \\E_2 &\equiv -l\bar{w} + p\bar{y} + q\bar{z} - (-l\bar{w} + p\bar{y} + q\bar{z}) = 0, \\E_3 &\equiv m\bar{w} + p\bar{x} - r\bar{z} - (m\bar{w} + p\bar{x} - r\bar{z}) = 0, \\E_4 &\equiv n\bar{w} + q\bar{x} + r\bar{y} - (n\bar{w} + q\bar{x} + r\bar{y}) = 0.\end{aligned} \right\} \quad (13)$$

These equations may be looked upon as having been derived from equations (1) by the successive elimination of w, x, y , and z respectively. The four equations of set (13) are equivalent to only two independent equations as a consequence of condition (10). For example,

$$nE_2 = qE_1 - lE_4 \quad \text{and} \quad nE_3 = -rE_1 + mE_4.$$

From a slightly different point of view, a necessary and sufficient condition that the following group of homogeneous linear equations (which are those of set (13) re-written)

$$\left. \begin{aligned}lX + mY + nZ &= 0, \\-lW + pY + qZ &= 0, \\-mW - pX + rZ &= 0, \\-nW - qX - rY &= 0,\end{aligned} \right\}$$

shall have a solution other than $W=X=Y=Z=0$ is the vanishing of the determinant of the coefficients. This determinant is skew-symmetrical, its order is even, and it

equals $(lr - mq + np)^2$. Hence equation (10) is the required condition.

For sake of completeness attention should be called to the fact that, if desired, the coordinates w, x, y, z of the foot of the perpendicular dropped from the point (w', x', y', z') upon the plane may be obtained by eliminating m, μ , and μ' from the last two equations of set (5) and each of equations (4). The formulæ obtained may be written :

$$\left. \begin{aligned} w &= w' + [l(\beta F' - \beta' F) + m(\gamma F' - \gamma' F) + n(\delta F' - \delta' F)] / \sqrt{D}, \\ x &= x' + [-l(\alpha F' - \alpha' F) + p(\gamma F' - \gamma' F) + q(\delta F' - \delta' F)] / \sqrt{D}, \\ y &= y' + [-m(\alpha F' - \alpha' F) - p(\beta F' - \beta' F) + r(\delta F' - \delta' F)] / \sqrt{D}, \\ z &= z' + [-n(\alpha F' - \alpha' F) - q(\beta F' - \beta' F) - r(\gamma F' - \gamma' F)] / \sqrt{D}, \end{aligned} \right\} \quad (14)$$

or

$$\left. \begin{aligned} w &= w' - lE'_2 + mE'_3 + nE'_4, \\ x &= x' + lE'_1 + pE'_3 + qE'_4, \\ y &= y' + mE'_1 + pE'_2 + rE'_4, \\ z &= z' + nE'_1 + qE'_2 - rE'_3, \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (15)$$

where

$$\begin{aligned} E'_1 &\equiv lX' + mY' + nZ', \\ E'_2 &\equiv -lW' + pY' + qZ', \\ E'_3 &\equiv mW' + pX' - rZ', \\ E'_4 &\equiv nW' + qX' + rY'. \end{aligned}$$

Obviously it should be possible to deduce formula (12) by substituting in equation (2) the expressions given by equations (15) for $w - w'$, $x - x'$, $y - y'$, and $z - z'$. As a matter of fact, this substitution, followed by appropriate use of condition (9), leads to

$$\begin{aligned} &(E'_1)^2 + (E'_2)^2 + (E'_3)^2 + (E'_4)^2 - \Delta_0^2 \\ &= (-pE'_1 + mE'_2 + lE'_3)^2 + (-qE'_1 + nE'_2 + lE'_4)^2 \\ &\quad + (rE'_1 + nE'_3 - mE'_4)^2 + (rE'_2 + qE'_3 - pE'_4)^2. \end{aligned} \quad (16)$$

Replacing E'_1, E'_2, E'_3 , and E'_4 in the parentheses of equation (16) by their respective values in terms of W', X', Y' , and Z' , and then making use of condition (10), it is found that the right-hand member of equation (16) vanishes, thus leaving formula (12). Nevertheless, the method given first is to be preferred, since it leads directly to formula (6) and since it is susceptible of generalization to n -dimensional linear space.

(b) The ground is now prepared for the solution of the main problem of the paper, which belongs to the domain of the Method of Least Squares, namely: to determine a two-dimensional plane in four-space so as to make the sum of the squares of the lengths of the perpendiculars dropped upon the plane from any (sufficiently large) number of given points a minimum.

Let the number of points outside the plane be κ (> 3), and let the i th point be symbolized by (w_i, x_i, y_i, z_i) , where $i=1, 2, \dots, \kappa$. Also, let ϕ denote the sum of the squares of the perpendiculars in question. Then, by formula (12),

$$\phi \equiv \sum_1^{\kappa} \Delta_i^2 = \sum_1^{\kappa} [(nW_i + qX_i + rY_i)^2 + (lX_i + mY_i + nZ_i)^2 + (pY_i + qZ_i - lW_i)^2 + (-rZ_i + mW_i + pX_i)^2],$$

. . . (17)

where

$$W_i \equiv \bar{w} - w_i, \quad X_i \equiv \bar{x} - x_i, \quad Y_i \equiv \bar{y} - y_i, \quad Z_i \equiv \bar{z} - z_i.$$

ϕ is to be a minimum with respect to the ten quantities $\bar{w}, \bar{x}, \bar{y}, \bar{z}, l, m, n, p, q, r$.

$\frac{\partial \phi}{\partial \bar{w}} = 0, \quad \frac{\partial \phi}{\partial \bar{x}} = 0, \quad \frac{\partial \phi}{\partial \bar{y}} = 0, \quad \frac{\partial \phi}{\partial \bar{z}} = 0$ lead to the following equations in the order given:—

$$\begin{aligned} (l^2 + m^2 + n^2) W'' + (mp + nq) X'' - (lp - nr) Y'' - (lq + mr) Z'' &= 0 \\ (mp + nq) W'' + (l^2 + p^2 + q^2) X'' + (lm + qr) Y'' + (ln - pr) Z'' &= 0 \\ -(lp - nr) W'' + (lm + qr) X'' + (m^2 + p^2 + r^2) Y'' + (mn + pq) Z'' &= 0 \\ -(lq + mr) W'' + (ln - pr) X'' + (mn + pq) Y'' + (n^2 + q^2 + r^2) Z'' &= 0 \end{aligned}$$

where

$$W'' \equiv \bar{w} - (\Sigma w)/\kappa, \quad X'' \equiv \bar{x} - (\Sigma x)/\kappa, \quad Y'' \equiv \bar{y} - (\Sigma y)/\kappa, \quad Z'' \equiv \bar{z} - (\Sigma z)/\kappa$$

Equations (18) are always satisfied when

$$W'' = X'' = Y'' = Z'' = 0,$$

that is, when

$$w = (\Sigma w)/\kappa, \quad \bar{x} = (\Sigma x)/\kappa, \quad \bar{y} = (\Sigma y)/\kappa, \quad \bar{z} = (\Sigma z)/\kappa;$$

hence the theorem: The minimum (or maximum) plane always passes through the centroid of the set of given points (w_i, x_i, y_i, z_i) .

Substituting the values of $\bar{w}, \bar{x}, \bar{y}, \bar{z}$ in equation (17), squaring the parenthetical expressions, and performing

the remaining summations with respect to the subscript i gives

$$\begin{aligned}\theta = & (\sigma_{11} + \sigma_{22})l^2 + (\sigma_{11} + \sigma_{33})m^2 + (\sigma_{11} + \sigma_{44})n^2 + (\sigma_{22} + \sigma_{33})p^2 \\ & + (\sigma_{22} + \sigma_{44})q^2 + (\sigma_{33} + \sigma_{44})r^2 + 2\sigma_{23}lm + 2\sigma_{24}ln \\ & - 2\sigma_{13}lp - 2\sigma_{14}lq + 2\sigma_{34}mn + 2\sigma_{12}mp - 2\sigma_{14}mr \\ & + 2\sigma_{12}nq + 2\sigma_{13}nr + 2\sigma_{34}pq - 2\sigma_{24}pr + 2\sigma_{23}qr, \quad (19)\end{aligned}$$

where

$$\begin{aligned}\theta & \equiv \kappa\phi, \quad \sigma_{11} \equiv \kappa\Sigma(w^2) - (\Sigma w)^2, \quad \sigma_{22} \equiv \kappa\Sigma(x^2) - (\Sigma x)^2, \dots, \\ \sigma_{12} & \equiv \kappa\Sigma(w_ix_i) - (\Sigma w)(\Sigma x), \dots, \\ \sigma_{34} & \equiv \kappa\Sigma(y_iz_i) - (\Sigma y)(\Sigma z); \quad \sigma_{ij} = \sigma_{ji}.\end{aligned}$$

A σ having equal subscripts is essentially positive for real values of the coordinates, since

$$\kappa\Sigma(t^2) - (\Sigma t)^2 = \Sigma(t_i - t_j)^2, \quad i < j.$$

Differentiating equations (19), (10), and (9), and putting $d\theta=0$ leads to

$$\left. \begin{aligned}B_1dl + B_2dm + B_3dn + B_4dp + B_5dq + B_6dr &= 0, \\ rdl - qdm + pdn + ndp - mdq + ldr &= 0, \\ ldl + mdm + ndn + pdp + qdq + rdr &= 0,\end{aligned} \right\} \quad (20)$$

where

$$\begin{array}{llllll}(\sigma_{11} + \sigma_{22})l & + \sigma_{23}m & + \sigma_{24}n & - \sigma_{13}p & - \sigma_{14}q, & \\ \sigma_{23}l + (\sigma_{11} + \sigma_{33})m & + \sigma_{34}n & + \sigma_{12}p & & - \sigma_{14}r, & \\ \sigma_{24}l & + \sigma_{34}m + (\sigma_{11} + \sigma_{44})n & & + \sigma_{12}q & + \sigma_{13}r, & \\ -\sigma_{13}l & + \sigma_{12}m & + (\sigma_{22} + \sigma_{33})p & + \sigma_{34}q & - \sigma_{24}r, & \\ -\sigma_{14}l & & + \sigma_{12}n & + \sigma_{34}p + (\sigma_{22} + \sigma_{44})q & + \sigma_{23}r, & \\ & - \sigma_{14}m & + \sigma_{13}n & - \sigma_{24}p & + \sigma_{23}q + (\sigma_{33} + \sigma_{44})r. & \\ & & & & \dots & (21)\end{array}$$

Multiply the first, second, and third equations of set (20) by 1, $-\xi$, and $-\eta$ respectively, add the products, and equate to zero the complete coefficients of the six differentials to obtain

$$\left. \begin{aligned}r\xi + l\eta &= B_1, & n\xi + p\eta &= B_4, \\ -q\xi + m\eta &= B_2, & -m\xi + q\eta &= B_5, \\ p\xi + n\eta &= B_3, & l\xi + r\eta &= B_6.\end{aligned} \right\} \quad (22)$$

Form the sum of the products obtained by multiplying

each equation of set (22) by the respective coefficient of ξ to find, by the aid of expressions (21), that

$$(l^2 + m^2 + n^2 + p^2 + q^2 + r^2)\xi + 2(lr - mq + np)\eta \\ = (lr - mq + np)(\sigma_{11} + \sigma_{22} + \sigma_{33} + \sigma_{44});$$

hence, by virtue of conditions (9) and (10), $\xi = 0$.

Next form the sum of the products obtained by multiplying each equation of group (22) by the respective coefficient of η to find, by referring to (9), (19), and (21), that $\eta = \theta$. Hence equations (22) reduce to

$$\left. \begin{aligned} B_1 - l\theta &= 0, & B_4 - p\theta &= 0, \\ B_2 - m\theta &= 0, & B_5 - q\theta &= 0, \\ B_3 - n\theta &= 0, & B_6 - r\theta &= 0. \end{aligned} \right\} \dots (23)$$

Equations (23) are homogeneous and linear in the six direction-ratios l, m, n, p, q, r , so that a necessary and sufficient condition for a non-trivial solution is

| | | | | | |
|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|--------------------------------------|
| $\sigma_{11} + \sigma_{22} - \theta,$ | $\sigma_{23},$ | $\sigma_{24},$ | $-\sigma_{13},$ | $-\sigma_{14},$ | 0 |
| $\sigma_{23},$ | $\sigma_{11} + \sigma_{33} - \theta,$ | $\sigma_{34},$ | $\sigma_{12},$ | $0,$ | $-\sigma_{14}$ |
| $\sigma_{24},$ | $\sigma_{34},$ | $\sigma_{11} + \sigma_{44} - \theta,$ | $0,$ | $\sigma_{12},$ | σ_{13} |
| $-\sigma_{13},$ | $\sigma_{12},$ | $0,$ | $\sigma_{22} + \sigma_{33} - \theta,$ | $\sigma_{34},$ | $-\sigma_{24}$ |
| $-\sigma_{14},$ | $0,$ | $\sigma_{12},$ | $\sigma_{34},$ | $\sigma_{22} + \sigma_{44} - \theta,$ | σ_{23} |
| $0,$ | $-\sigma_{14},$ | $\sigma_{13},$ | $-\sigma_{24},$ | $\sigma_{23},$ | $\sigma_{33} + \sigma_{44} - \theta$ |

When expanded condition (24) would be a complete equation of the sixth degree in θ . The solution of this equation, especially in numerical cases, is very greatly facilitated by the remarkable property that a certain linear transformation removes all the terms of odd degree and thus reduces the solution to that of an equation of the third degree. The way in which this reduction may be effected will now be explained.

(c) Let τ denote the mean value of all the trinomial elements constituting the principal diagonal of the determinant in equation (24), that is:

$$\tau \equiv 1/2(\sigma_{11} + \sigma_{22} + \sigma_{33} + \sigma_{44}) - \theta. \quad \dots (25)$$

Also let

$$\left. \begin{aligned} s_1 &\equiv 1/2(\sigma_{11} + \sigma_{22} - \sigma_{33} - \sigma_{44}), \\ s_2 &\equiv 1/2(\sigma_{11} - \sigma_{22} + \sigma_{33} - \sigma_{44}), \\ s_3 &\equiv 1/2(\sigma_{11} - \sigma_{22} - \sigma_{33} + \sigma_{44}), \end{aligned} \right\} \dots (26)$$

Substitution of expressions (25) and (26) in the determinant of (24) gives

$$\begin{vmatrix}
 a & a' & b & b' & c & c' & d & d' & e & e' & f & f' \\
 s_1 + \tau & \sigma_{23} & \sigma_{24} & -\sigma_{13} & -\sigma_{14} & 0 & & & & & & \\
 \sigma_{23} & s_2 + \tau & \sigma_{34} & \sigma_{12} & 0 & -\sigma_{14} & & & & & & \\
 \sigma_{24} & \sigma_{34} & s_3 + \tau & 0 & \sigma_{12} & -\sigma_{13} & & & & & & \\
 -\sigma_{13} & \sigma_{12} & 0 & -s_3 + \tau & \sigma_{34} & \sigma_{24} & & & & & & \\
 -\sigma_{14} & 0 & \sigma_{12} & \sigma_{34} & -s_2 + \tau & \sigma_{23} & & & & & & \\
 0 & -\sigma_{14} & \sigma_{13} & -\sigma_{24} & \sigma_{23} & -s_1 + \tau & & & & & &
 \end{vmatrix} \equiv U(\tau).$$

In the last determinant substitute $-\tau$ for τ and then multiply the second and fifth rows and the first, third, fourth, and sixth columns by -1 to find that $U(-\tau) = U(\tau)$. Therefore $U(\tau)$ is an even function of τ , that is, a function of τ^2 , and $U(\tau) = 0$ may be written as

$$\tau^6 + a_2\tau^4 + a_4\tau^2 + a_6 = 0 \quad . \quad . \quad . \quad (27)$$

Formulae for the coefficients a_2 , a_4 , and a_6 may be obtained in the following manner:—Imagine five zero constituents written in each of the columns of the above determinant headed a' , b' , c' , d' , e' , and f' . Thus the columns of $U(\tau)$ are to be considered as composed of binomial constituents, the second term in each sum being either τ or zero. $U(\tau)$ may now be developed as the sum of sixty-four (2^6) determinants each of which comprises six of its monomial columns.

The fifteen determinants involving τ^4 may be indicated by the headings of the monomial columns in $U(\tau)$ as $abc'd'e'f'$, $ab'cd'e'f'$, $ab'c'de'f'$, $ab'c'd'e'f$, $a'bcd'e'f'$, $a'bc'de'f'$, $a'bc'd'e'f$, $a'bc'd'e'f$, $a'b'cde'f'$, $a'b'cd'e'f'$, $a'b'cd'e'f$, $a'b'c'def'$, $a'b'c'def$, $a'b'c'd'ef$. The evaluation of these determinants leads to

$$\begin{aligned}
 -a_2 = s_1^2 + s_2^2 + s_3^2 + 2(\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{14}^2 \\
 + \sigma_{23}^2 + \sigma_{24}^2 + \sigma_{34}^2). \quad . \quad (28)
 \end{aligned}$$

Hence, a_2 is essentially negative for real values of the co-ordinates of the given points.

In the same notation, the fifteen determinants involving τ^2 are $abcde'f'$, $abcd'e'f'$, $abcd'e'f$, $abc'de'f'$, $abc'de'f$, $abc'd'ef$, $ab'cde'f'$, $ab'cde'f$, $ab'cd'e'f'$, $ab'cd'e'f$, $a'bcd'e'f'$, $a'bcd'e'f$, $a'bcd'ef$, $a'bc'de'f'$, $a'bc'de'f$. From these it will be found that

$$\begin{aligned}
 a_4 = (s_1s_2 + \sigma_{14}^2 - \sigma_{23}^2)^2 + (s_1s_3 + \sigma_{13}^2 - \sigma_{24}^2)^2 + (s_2s_3 + \sigma_{12}^2 - \sigma_{34}^2)^2 \\
 + 2(\sigma_{12}s_1 + \sigma_{13}\sigma_{23} + \sigma_{14}\sigma_{24})^2 + 2(-\sigma_{34}s_1 + \sigma_{13}\sigma_{14} + \sigma_{23}\sigma_{24})^2 \\
 + 2(\sigma_{13}s_2 + \sigma_{12}\sigma_{23} + \sigma_{14}\sigma_{34})^2 + 2(-\sigma_{24}s_2 + \sigma_{12}\sigma_{14} + \sigma_{23}\sigma_{34})^2 \\
 + 2(\sigma_{14}s_3 + \sigma_{12}\sigma_{24} + \sigma_{13}\sigma_{34})^2 + 2(-\sigma_{23}s_3 + \sigma_{12}\sigma_{13} + \sigma_{24}\sigma_{34})^2. \\
 . \quad . \quad . \quad (29)
 \end{aligned}$$

Accordingly, a_4 is essentially positive for real values of the coordinates. On changing signs throughout the fifth row and the fifth column of $U(0)$ it becomes evident that the determinant is skew-symmetrical with respect to the negative diagonal. Hence a_6 must equal the negative of a perfect square; in fact,

$$a_6 = -[s_1 s_2 s_3 + (\sigma_{12}^2 - \sigma_{34}^2)s_1 + (\sigma_{13}^2 - \sigma_{24}^2)s_2 + (\sigma_{14}^2 - \sigma_{23}^2)s_3 + 2(\sigma_{12}\sigma_{13}\sigma_{23} + \sigma_{12}\sigma_{14}\sigma_{24} + \sigma_{13}\sigma_{14}\sigma_{34} + \sigma_{23}\sigma_{24}\sigma_{34})]^2. \quad (30)$$

The conditions under which the preceding analysis "fails" will not be investigated in this paper, because they depend upon very special distributions of the given points. Such cases afford no difficulty, for they mean simply that no minimum plane exists. Analogous conditions present themselves in three-space, for illustration, when the associated ellipsoid having three unequal axes degenerates into a spheroid or a sphere. Cases of this kind would not arise when the residuals are small enough to justify employing the Method of Least Squares for the determination of the parameters in the equations of the plane.

(d) As a concrete illustration of the foregoing theory, the following data may be used:—(0, 0, 0, 0), (1, 1, 1, -1), (2, 1, -1, 0), (1, -1, 1, 2), (1, 2, -1, -1), (2, -1, 1, -1), (0, -1, -1, 1). These seven points have been chosen so that no five of them lie in the same hyperplane. It follows that $\sigma_{11}=28$, $\sigma_{22}=62$, $\sigma_{33}=42$, $\sigma_{44}=56$, $\sigma_{12}=7$, $\sigma_{13}=7$, $\sigma_{14}=-14$, $\sigma_{23}=-21$, $\sigma_{24}=-35$, $\sigma_{34}=0$, $s_1=-4$, $s_2=-24$, $s_3=-10$, $\kappa=7$, $\bar{w}=1$, $\bar{x}=1/7$, $\bar{y}=\bar{z}=0$. Substituting in formulas (28), (29), and (30), it will be found that

$$(\tau^2)^3 - 4612(\tau^2)^2 + 4438236(\tau^2) - 1177862400 = 0.$$

Approximate values of the roots of this cubic are

$$\tau_1^2 = 3412.5946, \quad \therefore \tau_1 = \pm 58.4174,$$

$$\tau_2^2 = 720.0844, \quad \therefore \tau_2 = \pm 26.8344,$$

$$\tau_3^2 = 479.3210, \quad \therefore \tau_3 = \pm 21.8934,$$

with $\theta = 94 - \tau$. The minimum value of θ obviously corresponds to the positive value of τ_1 . Substitution of this value of θ in equations (23) led to the following five ratios:

$$\frac{m}{l} = 0.7826, \quad \frac{n}{l} = 0.8641, \quad \frac{p}{l} = 0.3213, \quad \frac{q}{l} = -0.3922,$$

$$\frac{r}{l} = -0.5845.$$

Relation (9) now furnishes

$$\begin{aligned} l &= +0.58145, & p &= +0.1868, \\ m &= +0.4550, & q &= -0.2280, \\ n &= +0.5024, & r &= -0.3399. \end{aligned}$$

The following approximate values for the perpendicular distances between the seven given points and the minimum plane were computed by means of formula (12) :—

$$\begin{aligned} \Delta_1 &= 0.8932, & \Delta_4 &= 0.9638, \\ \Delta_2 &= 0.8333, & \Delta_5 &= 0.1540, \\ \Delta_3 &= 1.1785, & \Delta_6 &= 0.8505, \\ \Delta_7 &= 0.7254. \end{aligned}$$

Incidentally the coordinates of the foot of the perpendicular dropped from the origin upon the minimum plane were calculated by the aid of equations (15) to be approximately $w = +0.79335$, $x = +0.0311$, $y = -0.2305$, $z = +0.3381$. Finally, the equations of the minimum plane may be taken as

$$\begin{aligned} 4550w + 1868x + 3399z - 4817 &= 0 \\ 5815x + 4550y + 5024z - 831 &= 0 \end{aligned}$$

In conclusion, the writer desires to call attention to an interesting by-product of the preceding analysis. Since $\theta = \kappa\phi$ and ϕ denotes the sum of the squares of the perpendicular distances from the κ points of the given system to the plane, it follows that if all these points were to become co-planar then θ would equal zero and, conversely, if all the coordinates are real and $\theta = 0$ all the points will lie in a single plane. [If the points become collinear they may still be considered co-planar, although the plane may be indeterminate.] Therefore a necessary and sufficient condition that any number of real points shall lie in a plane in four-space is the vanishing of the determinant obtained by putting $\theta = 0$ in the left-hand side of equation (24). [For sake of elegance, change signs throughout the fifth row and the fifth column.]

Obviously a complete set of criteria for the order of the linearity of a system of points in four-space is afforded by the constant terms in the " θ -equations" for the hyperplane, the plane (*vide supra*), and the straight line. The author is now engaged in the complete generalization of the preceding problem to a k -flat in an n -flat, $k < n$.

CXXVIII. *Applications of the Correspondence Principle to the Theory of Line-intensities in Band-spectra.* By R. H. FOWLER*.

§ 1. *INTRODUCTION*.—The object of this paper is to present the theoretical laws governing the intensities of the lines in any single band, so far as these can yet be based on applications of the Correspondence Principle. It will be found that certain quantitative deductions can be drawn with considerable certainty. The work consists in a natural extension to these spectra of the ideas of Heisenberg †, which have proved so successful in interpreting the quantitative intensity theory of atomic spectra of “the first rank” ‡. The resulting formulæ are compared with the existing experimental material, and appear to be in satisfactory agreement, but the material for comparison is hardly yet quantitatively reliable. Certain subsidiary discrepancies remain which may be highly significant.

By way of introduction it is convenient to summarize here those applications of the Correspondence Principle which have special reference to band-spectra, and to stress their typical resemblances. It is in this way perhaps easier to see that they form a corporate whole. In the first instance, as is well known, the Correspondence Principle asserts, on account of the asymptotic equality of frequencies for large quantum numbers, a similar asymptotic equality between the intensities and polarizations of the light radiated by atoms (or molecules) according to the classical and the quantum theories. This assertion is unambiguous and quantitative. Outside the region of large quantum numbers the switches of the quantum theory can still be unambiguously related to terms in the Fourier development of the electrical moment of the atom (or molecule), and the frequencies of the light emitted according to the quantum theory can still be quantitatively described in terms of the mechanical motions. It is, however, only possible in general to postulate a qualitative correspondence between the probabilities of quantum switches and the Fourier coefficients, and so only a qualitative connexion between intensities and polarizations in the two theories. The lack of any more quantitative general correspondence is natural enough, and in fact essential, since the response of atoms to radiation, whether or not described in

* Communicated by the Author.

† Heisenberg, *Zeit. für Phys.* xxxi. p. 617 (1925).

‡ Landé, “*erster stufe*.”

terms of virtual oscillators, can only be connected in a symbolical way with the mechanical motions in the stationary states.

One significant exception has been recognized from the first *—that the complete absence of particular terms of the Fourier series may be taken to imply that the corresponding switches of the quantum theory never occur with emission or absorption of radiation (or only with certain polarizations). Their probabilities (or some of their component probabilities) are exactly zero. Such an application—valid for all quantum numbers and not merely asymptotically—will be described as *refined*. This first refined application is of course of particular importance in band-spectra, for progress in their theory would have been entirely impossible without the resulting selection rule $\Delta m = \pm 1$ or $\Delta m = 0, \pm 1$ for changes of the rotational quantum number m . The argument in this refined application may be stated thus:—On the classical theory the atom would *never* emit or absorb radiation of such and such frequencies. It must therefore be presumed that the corresponding quantum switches will *never* occur.

Quite recently it has been shown, especially by Heisenberg, that other such refined applications can be made. The simplest and most certain of these is the one required in the present paper. On the classical theory an atom, of the usual lightly coupled core-series-electron type, will emit radiation of a *total* amount which does *not* depend on the angle between the plane of the orbit of the series electron and the axis of resultant angular momentum. [The intensities of the various components in the light will of course depend notably on this angle.] It must therefore be expected that the corresponding *total* emission in the quantum theory will *not* depend on this angle—*i. e.* not depend on the third quantum number j . [The independence in this case is not absolutely exact on the classical theory; it would be in default by quantities of the extremely small order ω_j/ω_n compared with 1, where ω_j is the precessional frequency of the orbital plane, and ω_n the frequency of the electron in its quasi-Keplerian orbit, but one must believe that this is trivial.] This refined application leads at once, as Heisenberg has shown, to the exact Ornstein-Burger-Dorgelo † summation rules. In the hands of Kronig ‡ (in conjunction

* Bohr, *Danske Vid. Selsk. Skrifter*, iv. p. 16 (1918).

† *Zeit. für Phys.* xxiii. p. 258; xxiv. p. 24; xxviii. p. 135; xxix. p. 241 (1924).

‡ Kronig, *Zeit. für Phys.* xxxi. p. 885 (1925).

with a normal asymptotic application) it has yielded complete exact rules for the intensity ratios of all the lines in any multiplet [other than intercombinations] in any spectrum of the first rank, and of all their Zeeman components in weak and strong fields. Theory and experiment appear to be in full agreement, though a wider range of experimental material is required*.

The common idea underlying these refined applications is that when classical theory demands unambiguously a certain null effect, then the quantum theory also must provide for a similar null effect; whereas when there is a certain positive effect in the classical theory there will be some positive effect in the quantum theory which need only (and generally will only) be asymptotically the same for large quantum numbers. It is evident that a similar refined application can be made to the theory of line-intensities in band-spectra—put simply, that the Ornstein-Burger-Dorgelo summation rules must hold for the lines of a single band, other than a pure rotation band, just as for the lines of a single multiplet. The rest of this paper will be concerned with the formal development of these rules in various cases and their comparison with observations. The rules themselves are probably more reliable than our theoretical knowledge of the weights of the various molecular states, at least in certain cases, and a quantitative study of line intensities in a band may well throw light on these and other points in molecular structure.

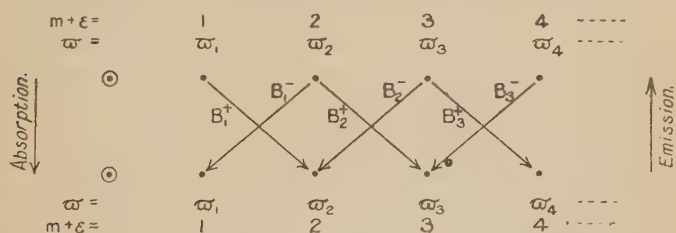
With regard to the experimental facts, the general symmetry of the observed intensities of the lines in the positive and negative branches of a band is well known. It is found both in infra-red absorption bands (*e. g.* HCl) and in the more complicated bands in the visible region (*e. g.* “Cyanogen” bands)†. The intensities of the lines increase regularly from the beginning of the branches, attain a maximum intensity and then fade away. The position of the maximum on the branch exhibits a well-recognized dependence on temperature, which has even been tentatively employed as an index of the temperature of stellar reversing

* Besides the refined applications relevant here, two other such applications, equally interesting, have been proposed by Heisenberg (*loc. cit.*), one to the problem of spectroscopic continuity, and the other to the state of polarization of scattered and resonance radiation, and the experiments of Wood and Ellett. These can only be mentioned in passing, but they appear strongly to confirm the validity of the whole idea on which refined applications are based.

† Sommerfeld, *Atombau u. Spektrallinien*, ed. 4, pp. 711, 722–4.

layers *. The theory of these intensities has recently been taken up by Kemble †, who has pointed out the apparent difficulty that the first pair of lines in the positive and negative branches of a band are now normally classified as due to the (absorption) switches $\frac{1}{2} \rightarrow \frac{3}{2}$ and $\frac{3}{2} \rightarrow \frac{1}{2}$ respectively in rotational quantum number ‡. It is not immediately obvious that there is any theoretical reason, *purely on grounds of symmetry*, for the equality in strength of these two lines. Kemble experiments with various solutions, and decides in favour of one which is in substantial agreement with experiment, and is based on a tentative application of the Correspondence Principle, in essentials the same as that established by Heisenberg and described above. It will be one object of this paper to bring Kemble's suggestion into its proper relationship with other refined applications of the Correspondence Principle, and to show that unambiguous results can be reached practically without calculation.

§ 2. *Band structure*.—An adequate model for the discussion of the structure of a simple band or set of bands is the oscillating-rotating dipole. It follows at once, by the old refined application of the Correspondence Principle, that the selection rule for m is $\Delta m = \pm 1$. A null branch, $\Delta m = 0$, can only occur if the molecule has an electric moment along its axis of rotation. In no circumstances can this model or the generalizations of Kramers and Pauli § lead to any selection rule more general than $\Delta m = 0, \pm 1$. For any model the structure of a simple band with no zero branch is now usually represented formally as under. The arrows



represent the various absorption switches in m , and the $B_n \pm$ against them the relative molecular absorption probabilities ||.

* Birge, *Astrophys. J.* lv. p. 273 (1922).

† Kemble, *Phys. Rev.* xxv. p. 1 (1925).

‡ Sommerfeld, *loc. cit.* p. 712.

§ Kramers & Pauli, *Zeit. für Phys.* xiii. p. 351 (1923).

|| Different suffix letters, n and m , will be deliberately used for lines and states. This may help to avoid confusion.

It is assumed that the initial and final states can be paired in such a way that for any pair both m and ϖ are equal. This follows for any simple model from the principles of the quantum theory, and may be true in general. On any simple theory we must also expect that

$$\varpi_m \propto m + \epsilon + \alpha \quad (\varpi_1 \propto 1 + \alpha, \text{ etc.}),$$

where α is constant. [For simple dipoles α is probably either $-\frac{1}{2}$ or 0. It can be left indefinite in the following arguments.] The relative numbers of molecules in the various initial states in statistical equilibrium will be proportional to

$$\varpi_m e^{-\delta m^2/T}, \dots \dots \dots (1)$$

where δ is (roughly) constant and T is the absolute temperature. [This formula will be slightly modified on the theory of Kramers and Pauli.]

§ 3. *The Summation Rules, and the relative Absorption Coefficients.*—To make the necessary further refined application of the Correspondence Principle, we have only to observe that on the classical theory the total reaction of the oscillating-vibrating dipole (or similar model) to radiation must to a close approximation be independent of the rotational quantum number m . This will be true so long as the frequency of rotation σ is very small compared with the vibration frequency ω , and so long as the centrifugal force does not appreciably affect the vibrational motion, which is secured by the same condition. The deviations from equality must be expected to be of the order σ/ω compared with 1, so that the equality will hold so long as m is not too large. It follows at once, by a refined application, that, so long as we may ignore differences of wave-length among the switches,

$$B_1^+ = B_1^- + B_2^+ = B_2^- + B_3^+ = \dots \dots \dots (2)$$

A second set of equations is obtained by the application of the same argument to the process of emission. Denote the corresponding molecular emission coefficients by A_n^\pm . Then

$$A_1^- = A_1^+ + A_2^- = A_2^+ + A_3^- = \dots \dots \dots (3)$$

The A_n^\pm and B_n^\pm are (or are proportional to) Einstein's probability coefficients, and according to his well-known analysis satisfy the equations

$$\frac{8\pi h\nu^3}{c^3} \varpi_n B_n^+ = \varpi_{n+1} A_n^+, \quad \frac{8\pi h\nu^3}{c^3} \varpi_{n+1} B_n^- = \varpi_n A_n^- \quad (4)$$

Again ignoring differences of wave-length, equation (4) indicates that for each switch

$$\varpi_n B_n^+ / \varpi_{n+1} A_n^+ \text{ or } \varpi_{n+1} B_n^- / \varpi_n A_n^-$$

is constant. To put these equations in symmetrical form, let us write

$$\varpi_n B_n^+ = b_n^+, \quad \varpi_{n+1} B_n^- = b_n^-. \quad . \quad . \quad . \quad (5)$$

The b_n^\pm then denote the product of the molecular absorption probabilities in any state by the weight of that state, and in terms of the b_n^\pm the equations (2) and (3) can be written *

$$\frac{b_1^+}{\varpi_1} = \frac{b_1^- + b_2^+}{\varpi_2} = \frac{b_2^- + b_3^+}{\varpi_3} = \dots = X, \quad . \quad (6)$$

$$\frac{b_1^-}{\varpi_1} = \frac{b_1^+ + b_2^-}{\varpi_2} = \frac{b_2^+ + b_3^-}{\varpi_3} = \dots = Y. \quad . \quad (7)$$

Relative absorption coefficients for the different lines are given by the ratios of the b_n^\pm multiplied by the exponential factors only from (1).

Equations (6) and (7) suffice to determine all the b_n^\pm in terms of X and Y, but do not immediately determine the ratio X/Y itself. If we solve (6) and (7) for b_n^\pm we find

$$\begin{aligned} b_n^+ &= (\varpi_n + \varpi_{n-2} + \dots)X - (\varpi_{n-1} + \varpi_{n-3} + \dots)Y \\ b_n^- &= (\varpi_n + \varpi_{n-2} + \dots)Y - (\varpi_{n-1} + \varpi_{n-3} + \dots)X \end{aligned} \quad (8)$$

Hence if any pair of b_n are equal, then $X=Y$ and all pairs of b_n must be equal. That X and Y must in general be equal can be inferred in several ways, of which the most fundamental seems to rest on a further refined application of the Correspondence Principle. We have already seen in this way that the total radiative activity of any state of the molecule must not depend on the rotation. Suppose the molecule can be reduced to rest and possesses two vibrational states. There will be certain probabilities for the switches to and from these states, connected by Einstein's equations. Its total radiative activity must, however, be the same as if it were rotating, and the same relation must therefore hold between the probability coefficients, although in the rotating states these are no longer paired together. If we form Einstein's equation for the non-rotating states in the notation of equations (6) and (7), we find $b' = b''$. By the refined

* These arguments form of course the general basis for the interpretation of the rules of Ornstein, Burger, and Dorgelo. They have been repeated here in detail, particularly to stress the independence of (6) and (7) of temperature, which is far more important here than in the theory of atomic spectra.

application of the Correspondence Principle here in question, we must have $b' = b_1^+$ and $b'' = b_1^-$, so that $b_1^+ = b_1^-$, and therefore $X = Y$ etc., as above.

This argument is somewhat unusual, and it is comforting to confirm it by other arguments, formally simpler but less direct. The asymptotic equality of pairs of b_n in the limit of large n can be inferred from an ordinary application of the Correspondence Principle. This implies $X = Y$. Again, using $\varpi_n = n + \alpha$, we find

$$\left. \begin{aligned} b_{2n}^+ &= n(n + \alpha)(X - Y) + nX, \\ b_{2n}^- &= n(n + \alpha)(Y - X) + nY. \end{aligned} \right\} \quad \dots \quad (9)$$

There is therefore an algebraic necessity for $X = Y$, for otherwise, for sufficiently large n , we arrive at impossible negative intensities. We conclude that

$$\left. \begin{aligned} b_{2n}^+ &= b_{2n}^- = nX = \frac{1}{2}(\varpi_{2n} - \alpha)X, \\ b_{2n-1}^+ &= b_{2n-1}^- = (n + \alpha)X = \frac{1}{2}(\varpi_{2n-1} + \alpha + 1)X. \end{aligned} \right\} (\varpi_n = n + \alpha). \quad \dots \quad (10)$$

The actual relative absorption coefficients α_n^\pm will be given by multiplying the b_n^\pm of (10) by the temperature factor. Thus

$$\left. \begin{aligned} \alpha_{2n}^+ &= nX e^{-\delta(2n-2\epsilon)^2/T}, & \alpha_{2n-1}^+ &= (n + \alpha)X e^{-\delta(2n-1-2\epsilon)^2/T}, \\ \alpha_{2n}^- &= nX e^{-\delta(2n+1-2\epsilon)^2/T}, & \alpha_{2n-1}^- &= (n + \alpha)X e^{-\delta(2n-2\epsilon)^2/T}. \end{aligned} \right\} \quad (11)$$

§ 4. *Infra-red bands, in particular of HCl.*—If $\alpha = -\frac{1}{2}$, and variations of wave-length are ignored (the theory can hardly be extended so far as to make their inclusion significant), formula (10) gives b_n^\pm a sequence of values proportional to 2, 4, 6, 8, If $\alpha = 0$ the sequence is 4, 4, 8, 8, 12, 12, By an argument based as stated on the same fundamental idea, but differing in detailed development*, Kemble arrives at a formula [(21) of his paper] for the absorption coefficients, equivalent to (10) and (11) here if the b_n^\pm have the sequence of values 3, 5, 7, 9, He has further shown that his formula is in substantial agreement with the observations on the main band of HCl at 3.5μ . The observations could hardly distinguish between Kemble's sequence of b_n^\pm and the sequence 2, 4, 6, 8, or perhaps even 4, 4, 8, 8, 12, 12, The present theory may therefore be taken to be equally in agreement with experiment. There are no outstanding discrepancies, in particular none for the first pair of lines, and the positions

* I do not think that Kemble's development can be maintained against the more direct development of this paper.

of the lines of maximum intensity are properly predicted not only for this band but also for the overtone band at 1.7μ and for the bands of HF and HBr. It will be observed that the predicted line intensities are slightly asymmetrical owing to the temperature factor; in cases of absorption such as these $\alpha_n^+ > \alpha_n^-$. *The absorption line of shorter wave-length should be stronger, by a factor depending on the temperature, than the corresponding line of longer wave-length in the other branch.* In the usual terminology, in absorption the positive branch should be stronger than the negative.

It must not be forgotten, a point brought out by Kemble, that the observations give total percentage absorptions by a given length of absorbing gas, so that except when these percentages are less than 20 or at most 30, they cannot be directly compared with atomic absorption coefficients. A detailed study of the temperature variation of the relative intensities of the HCl and other absorption bands, especially when the total absorption is never allowed to get too high, might provide information of interest. It hardly seems possible in view of the success of similar refined applications of the Correspondence Principle in other fields to doubt the correctness of equations (11) for not too large n if the assumed structure of § 2 is correct.

When we attempt to compare the observations on other infra-red bands * with equations (11), especially in respect of the predicted asymmetry, we meet with grave anomalies. I. In the overtone band of HCl at 1.75μ , the total absorption lies between 20 per cent. and 30 per cent. and favours a comparison with theory. The first pair of lines appear equal. In all other pairs except the 3rd, the line of shorter wave-length (the positive branch) is (apparently) the stronger, according to theory. The 3rd pair, of maximum intensity, is exceptional. II. In the band of HF at 2.5μ again the first pair are equal and the other pairs except the 2nd (maximum pair) stronger in the positive branch. The absorptions here, however, are rather high, running up to 90 per cent. III. In the band of HBr at 3.9μ the lines in the negative branch are uniformly stronger! If attention is paid only to the single maximum line, then in all these cases, including perhaps even the main band of HCl, one is tempted to say that the *negative* branch is the stronger, but I believe this generalization to be quite unwarranted by the observations recorded. There is, however, clearly occasion here for further interesting experimental work for comparison with theory.

* Imes, Astrophys. J. 1. p. 251 (1919).

Quantitative comparisons beyond those worked out by Kemble are hardly likely to be of value, except perhaps for the small absorptions in the overtone band of HCl. It follows at once from equations (11) that

$$\frac{\alpha_n^+}{\alpha_n^-} = e^{\delta(2n-2\epsilon+1)T}. \quad . \quad . \quad . \quad (11.1)$$

[For simplicity the most probable case $\epsilon = \frac{1}{2}$, $\alpha = -\frac{1}{2}$ will alone be considered.] It follows further that if n^\times is the value of n (not necessarily integral) for which the positive branch attains its maximum intensity, then

$$2\delta(n^\times)^2/T = 1. \quad . \quad . \quad . \quad (11.2)$$

Therefore

$$\frac{\alpha_n^+}{\alpha_n^-} = e^{n(n^\times)^2}. \quad . \quad . \quad . \quad (11.3)$$

For HCl as recorded by Imes, $n^\times = 3$. The computed and observed intensity ratios are as follows:—

| n . | Ratios. | |
|---------|---------|-------|
| | Obs. | Calc. |
| 1 | 1.0 | 1.1 |
| 2 | 1.15 | 1.2 |
| 3 | 0.95 | 1.4 |
| 4 | 1.3 | 1.5 |
| 5 | 1.25 | 1.7 |
| 6 | 1.25 | 1.8 |

The entries for the observed ratios are very rough, being obtained merely by reading off *maximum ordinates*. The greatest absorption is only 36 per cent. In spite of the deviations, which are of a type which must contain large experimental errors, there is no reason to believe in any systematic deviation from the theory. At least the sometimes expressed opinion that the negative branch (of longer wave-length) is the stronger is not borne out by these observations.

§ 5. *Visible bands, and bands with zero branches.*—Bands in the visible and ultra-violet regions are in general studied in emission, and in general the constant δ in equation (1) is very small. The temperature factor can only be sensible

for small m if the molecule contains at most one atom heavier than He. Moreover, the effective temperature of the emitting material will normally be controlled by the mean energy of the bombarding electrons and so in general be very high. The intensities of the earlier emission lines should therefore be effectively proportional to b_n^{\pm} . The intensities will be cut down to zero by the temperature factors later in the sequences. We should therefore get full symmetry in the *initial* intensities of the positive and negative branches of a band with no zero branch, which at first increase steadily along the branches according to the law (10). The general features of this intensity distribution are precisely those observed, but it will be interesting to know in detail whether the law (10), and if so for what value of α , is quantitatively observed in the early lines. If $\alpha = -\frac{1}{2}$ the early intensities will be in arithmetical progression. If $\alpha = 0$ they will be equal in pairs, and the pairs will be in such a progression. Such evidence as is available is discussed in § 6.

We can write down in a similar way some of these equations for the intensities in the more usual type of bands which contain zero branches, corresponding to $\Delta m = 0$. Let b_n^0 have the same meaning for the zero branch that b_n^{\pm} have for the other branches. Then

$$\left. \begin{aligned} \frac{b_1^0 + b_1^+}{\varpi_1} &= \frac{b_1^- + b_2^0 + b_2^+}{\varpi_2} = \frac{b_2^- + b_3^0 + b_3^+}{\varpi_3} = \dots = X, \\ \frac{b_1^- + b_1^0}{\varpi_1} &= \frac{b_2^- + b_2^0 + b_1^+}{\varpi_2} = \frac{b_3^- + b_3^0 + b_2^+}{\varpi_3} = \dots = Y. \end{aligned} \right\} \quad (12)$$

From the symmetry of these equations it is at once clear that if $b_n^+ = b_n^-$ for any value of n , then $X = Y$ and $b_n^+ = b_n^-$ for all values of n . We can again conclude by a refined application of the Correspondence Principle to a comparison of the rotating molecule with the molecule at rest that $b_1^+ = b_1^-$ and therefore that $X = Y$ etc., as before. The temperature factors in such bands are usually unimportant for early n 's. The theory thus still predicts the observed symmetry, and in addition the relations

$$\frac{b_1^0 + b_1^+}{\varpi_1} = \frac{b_2^0 + b_2^+ + b_1^-}{\varpi_2} = \frac{b_3^0 + b_3^+ + b_2^-}{\varpi_3} = \dots = X \quad (13)$$

between the intensities of the zero and the positive (or negative) branch.

It is clear that the equations above give the maximum information possible without more detailed molecular models.

The pictorial value of these is still somewhat uncertain, but perhaps the use of a particular model, and an attempt to proceed beyond equations (13), similar to Kronig's work, may not be entirely unfruitful. Let us consider the following model:—a quasi-rigid diatomic molecule, moving like a spinning-top, with an electronic moment of momentum $j\hbar/2\pi$ about the line of nuclei, in steady precessional motion about its invariable axis with a total moment of momentum $m\hbar/2\pi$ ($m > j$). The rigid body contains an electric moment (expressed in multiple Fourier Series) with components along the line of nuclei and along axes at right angles. Let the electric moment, when the line of nuclei of the molecule is at rest, have components X, Y, Z along axes fixed in space given by

$$X = \frac{1}{2} \sum_{\tau} X_{\tau} e^{2\pi i(\omega\tau)t}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

etc., where X_{τ} is a complex number and $X_{-\tau}$ its conjugate. The axis Z is the line of nuclei. Now suppose that the invariable axis R lies in the plane of Z and X and makes an angle θ with OZ , necessarily such that

$$\cos \theta = j/m. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Take a set of three instantaneous axes P, Q, R of which Q coincides with Y . Then the amplitudes of the electric moments along these axes are

$$R_{\tau} = Z_{\tau} \cos \theta + X_{\tau} \sin \theta,$$

$$Q_{\tau} = Y_{\tau},$$

$$P_{\tau} = -Z_{\tau} \sin \theta + X_{\tau} \cos \theta.$$

These axes are, however, rotating about OR with frequency σ . The electric moments $P_{\tau}^0, Q_{\tau}^0, R_{\tau}^0$, referred to axes fixed in space, momentarily coinciding with P, Q, R , are therefore

$$R_{\tau}^0 = Z_{\tau} \cos \theta + X_{\tau} \sin \theta,$$

$$P_{\tau}^0 + iQ_{\tau}^0 = (P_{\tau} + iQ_{\tau}) e^{-2\pi i\sigma t}$$

$$= \{(-Z_{\tau} \sin \theta + X_{\tau} \cos \theta) + iY_{\tau}\} e^{-2\pi i\sigma t}.$$

It follows that the squares of the amplitudes of the components of frequencies $(\omega\tau) \pm \sigma$ in both P and Q are respectively

$$\frac{1}{4} \{(-Z_{\tau} \sin \theta + X_{\tau} \cos \theta) \mp iY_{\tau}\}$$

$$\{-Z_{-\tau} \sin \theta + X_{-\tau} \cos \theta\} \pm iY_{-\tau} \}. \quad . \quad (16)$$

In evaluating this expression we must, however, remember that the invariable axis R may have any position whatever in the XY plane of the molecule and that the square of the

amplitude above must be averaged over all such positions to give the mean square amplitude for a number of atoms. This means that we must replace X_τ and Y_τ by zero, $X_\tau X_{-\tau}$ and $Y_\tau Y_{-\tau}$ by $\frac{1}{2}(X_\tau X_{-\tau} + Y_\tau Y_{-\tau})$, while $X_{-\tau} Y_\tau - X_\tau Y_{-\tau}$ is invariant.

The mean value of the expression (16) is therefore

$$\frac{1}{4}\{Z_\tau Z_{-\tau} \sin^2 \theta + \frac{1}{2}(X_\tau X_{-\tau} + Y_\tau Y_{-\tau})(1 + \cos^2 \theta) \\ \mp i(X_{-\tau} Y_\tau - X_\tau Y_{-\tau}) \cos \theta\}. \quad (17)$$

The mean square amplitude of the corresponding term of frequency $(\omega\tau)$ in R is the mean value of

$$(Z_\tau \cos \theta + X_\tau \sin \theta)(Z_{-\tau} \cos \theta + X_{-\tau} \sin \theta),$$

or

$$Z_\tau Z_{-\tau} \cos^2 \theta + \frac{1}{2}(X_\tau X_{-\tau} + Y_\tau Y_{-\tau}) \sin^2 \theta. \quad (18)$$

To the approximation which ignores the frequency differences between $(\omega\tau) \pm \sigma$ and $(\omega\tau)$, the rate of radiation of energy is proportional to the sum of the squared amplitudes, and is therefore independent, as it should be, of θ .

It is a deduction therefore from classical theory that the intensities in the positive, negative, and zero branches of a classical band should all be expressible in the form

$$Q(\cos \theta),$$

where Q is a quadratic. Since $\cos \theta = j/m$, we are therefore entitled (following Kronig) to assume that the molecular emission coefficients (Einstein's A's) can be expressed in the form

$$Q_1(m)/Q_2(m),$$

where Q_1 and Q_2 are both quadratic functions. We have, however, worked above in terms of b_n , where each b is proportional to the corresponding ϖA , ϖ being the weight of the state from which the emission switch A starts. Thus we are entitled to assert that, in the quantum theory, we shall find

$$\left. \begin{aligned} b_n^+ &= \varpi_{n+1} \frac{Q_1(n)}{Q_2(n)}, \\ b_n^- &= \varpi_n \frac{Q_1'(n)}{Q_2'(n)}, \\ b_n^0 &= \varpi_n \frac{Q_1''(n)}{Q_2''(n)}, \end{aligned} \right\} \dots \dots \dots (19)$$

all the Q 's being quadratics. Since we have already proved

that $b_n^+ = b_n^-$, we must have

$$\varpi_{n+1} \frac{Q_1(n)}{Q_2(n)} \equiv \varpi_n \frac{Q_1'(n)}{Q_2'(n)} \quad (\varpi_n = n + \alpha).$$

It follows that ϖ_n must be a factor of either Q_1 or Q_2' and similarly for ϖ_{n+1} ; all possibilities reduce to two,

$$b_n^\pm = \varpi_{n+1} \varpi_n \frac{L(n)}{Q(n)} \quad \text{or} \quad \frac{Q(n)}{L(n)}, \quad \dots \quad (20)$$

where $L(n)$ is a linear function. The form of b_n^0 must be left general, as in (19) above. We have to satisfy equations (13) with functions of the form (20). In the first case the form of $L(n)$ is determined by the initial condition that b_n^- must vanish for the first state ($b_0^- = 0$). We may suppose further that from the structure of the molecule and the Correspondence Principle we know the ratio b_n^0/b_n^+ (say $\kappa: \frac{1}{2}$) for large n . We can therefore assume

$$\left. \begin{aligned} b_n^\pm &= \frac{\frac{1}{2}(n + \alpha + 1)(n + \alpha)n}{(1 + \kappa)(n + A_1)(n + B_1)} X, \\ b_n^0 &= \frac{\kappa(n + \alpha)(n + C_2)(n + D_2)}{(1 + \kappa)(n + A_2)(n + B_2)} X. \end{aligned} \right\} \dots \quad (21)$$

There are then as many conditions to be satisfied as there are undetermined coefficients, and just *two* solutions of the equations (13) as an identity in n . This is easily verified. One of these is

$$b_n^\pm = \frac{\frac{1}{2}n}{1 + \kappa} X, \quad b_n^0 = \left\{ \frac{\kappa n + \frac{1}{2}}{1 + \kappa} + \alpha \right\} X \quad \dots \quad (22)$$

The other coincides with (22) when $\alpha = -\frac{1}{2}$. When $\alpha \neq -\frac{1}{2}$ neither solution is physically significant, since it is easily found that b_n^0 does not vanish with κ . That it must so vanish follows at once from the usual refined application of the Correspondence Principle. This however is to be expected, since when $\alpha \neq -\frac{1}{2}$ our original solution for no zero branch cannot be put into the form (19), for odd and even b 's must be represented by different formulæ. The second alternative in (20) requires us to assume that

$$\left. \begin{aligned} b_n^\pm &= \frac{\frac{1}{2}n(n + A_1)}{(1 + \kappa)(n + C_1)} X, \\ b_n^0 &= \frac{\kappa(n + \alpha)(n + A_2)(n + B_2)}{(1 + \kappa)(n + C_2)(n + D_2)} X. \end{aligned} \right\} \dots \quad (22')$$

The form of the factor n is determined by the initial condition. In this case there is one more unknown than condition, and there are two solutions, one of which is (22) and the other contains an arbitrary constant. This latter, however, reduces to (22) when $\alpha = -\frac{1}{2}$, and again when $\alpha \neq -\frac{1}{2}$ neither solution is physically significant. When $\alpha \neq -\frac{1}{2}$ we must therefore assume different forms for b_{2n}^{\pm} and b_{2n+1}^{\pm} . These can be treated in the same way and solutions obtained, but it does not seem desirable to pursue such speculations further until experimental material is available.

§ 6. *Comparison with observation on visible bands.*—(i.) *Iodine Bands.* R. W. Wood's* observations on the fluorescent spectrum of I_2 vapour under stimulus by the Hg green line provide a delicate test of part of the foregoing theory (when there is no zero band), for atoms are present in a single initial state and emit the lines $(n)^+$ and $(n+1)^-$ with intensities proportional to A_n^+ and A_{n+1}^- . There are no statistical complications. The intensities emitted must therefore by (4) and (5) be proportional to b_n^+ and b_{n+1}^- . The analysis of these observations by Lenz† shows that n lies between 8 and 10. The ratio of the intensities should theoretically be

$$\frac{b_8^+}{b_9^-} = \frac{4}{5+\alpha}, \quad \frac{b_9^+}{b_{10}^-} = \frac{5+\alpha}{5} \quad \text{or} \quad \frac{b_{10}^+}{b_{11}^-} = \frac{5}{6+\alpha}. \quad (\alpha=0, \text{ or } -\frac{1}{2}).$$

Wood states that under conditions free from subsequent reabsorption in the I_2 vapour all the pairs of fluorescent lines show equal intensities in every one of the 20 to 30 bands. The observations are probably in accord with theory for either value of α . The theory *might* demand a difference of as much as 10 per cent. in intensity in favour of the line of the negative branch (longer wave-length), which would scarcely have been recorded, as the lines do not appear to have been studied photometrically.

(ii.) *Other Emission Bands*‡. The experimental material

* R. W. Wood, Phil. Mag. xxxv. p. 236 (1918).

† Lenz, Phys. Zeit. xxi. p. 691 (1920).

‡ I believe that I have followed Sommerfeld and Kratzer (Sommerfeld, *loc. cit.*) in calling "positive" that branch whose corresponding lines are of shorter wave-length. This branch is, however, frequently called R, or negative. Danger of confusion will be avoided if the definition "branch of shorter wave-lengths" is consistently borne in mind.

available for discussion is as follows :—(A) An examination of intensities in the “Cyanogen band” $\lambda 3883$ by Birge*. He gives no details, but states that when $n^\times = 30.4$ the intensities in his spectrograms are well represented by the formula

$$\alpha_n = c_1 n^{3/2} e^{-c_2 n^3},$$

from $n=5$ to $n=137$, if c_2 is adjusted to give the correct n^\times . The intensity curves of the two branches are similar in shape, but the branch of longer wave-lengths (Heulinger’s P) is from 10 per cent. to 20 per cent. the more intense. The theoretical formula ($ne^{-c_2 n^3}$) is stated to give the position of the maximum correctly, but to give intensities five times too small at the end of the band. This band is difficult for intensity work owing to the close spacing of the lines. The intensity difference in the two branches is confirmed by Schwan†.

(B) Intensities in the band-spectrum of copper (probably CuH) are recorded by Frerichs‡. He gives intensity curves for the two branches of three bands with maxima at about $n^\times = 13, 14$. The intensities of the early lines of the two branches in these bands are closely equal, and increase regularly and apparently linearly with n (not like $n^{3/2}$), but intensity differences develop towards the maxima, and thereafter the branch of longer wave-lengths (Frerichs’ P) is uniformly the more intense. At the maxima the amounts as read from his figure 1 are 27 per cent., 13 per cent., and 11 per cent. Beyond the maxima the percentage difference seems to show a general tendency to go on increasing.

(C) Some intensities, which do not claim to be more than fragmentary, are recorded by Fassbender§ for two of the negative Nitrogen bands ($\lambda 3914, \lambda ?$). The initial linear increase in intensity seems well shown and the approximate initial equality in the branches. Maxima occur at about $n^\times = 10$, and the branch of longer wave-lengths is the more intense. The curves are not certain enough to give a quantitative intensity ratio.

To compare these results with the theory (for simplicity

* Birge, *loc. cit.*

† M. Schwan, *Diss. Bonn* (1923). Not available for reference. Quoted by Frerichs, see below.

‡ Frerichs, *Zeit. für Phys.* xx. p. 170 (1923–4).

§ Fassbender, *Zeit. für Phys.* xxx. p. 73 (1924).

with $\alpha = -\frac{1}{2}$, $\epsilon = \frac{1}{2}$) we have for emission

$$\alpha_n^+ = Xn e^{-\delta(n+\frac{1}{2})^2/T}, \quad \alpha_n^- = Xn e^{-\delta(n-\frac{1}{2})^2/T}, \quad . \quad (23)$$

$$\frac{\alpha_n^-}{\alpha_n^+} = e^{n(n^{\times})^2}. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

On the whole it appears as if the early lines have the proper sort of increase of intensity demanded by (10 or (13), but this conclusion must be tentative. On the other hand, the theory does definitely predict that the branch of *longer wave-length* should be the more intense *in emission* according to (24), and this is qualitatively in agreement with observation. For $n^{\times} = 13\frac{1}{2}$, equation (24) gives $7\frac{1}{2}$ per cent. instead of the 27, 13, 11 per cent. recorded above. For Birge's Cyanogen band with $n^{\times} = 30.4$ it gives 3.3 per cent. at the maximum, rising to 15 per cent. at the end of the band (observed 10 per cent. to 20 per cent.). The shape of the observed and theoretical intensity curves would not be in good agreement, but much distortion is possible in emission bands purely from distortions of statistical equilibrium on which the temperature factor in (23) is based.

One can rest fairly content with the general agreement on existing data in the hope of confirmation or refutation to come, but one fundamental point must be made. According to the present theory the branch of longer wave-lengths must be stronger in emission, the branch of shorter wave-lengths in absorption, owing solely to statistical temperature factors. Both these requirements are confirmed by observation, if my interpretation of the infra-red absorptions is accepted, but this is admittedly doubtful and can be, and has been, questioned*. If one branch is to be the stronger both in emission and absorption, this can only be due to unequal values of b_n^+ and b_n^- . I believe that it would then have to be concluded that the structure given in § 2 must be radically altered. If one branch really is stronger in emission and the other in absorption, then this must primarily be a statistical temperature effect, and must be investigated as such. Points such as these, however, cannot be usefully discussed further at this stage.

§ 7. *Kratzer's doublet theory.*—Kratzer has proposed a theory of bands in which it is necessary to distinguish between positive and negative values of m . Corresponding positive and negative values form close doublets, except for the first

* Frerichs, *loc. cit.* p. 178.

line of each branch which is single. It is at present doubtful what field of validity (if any) this theory has, but it may be noticed that the intensity theory of this paper has an immediate application to such bands. Equations (10) continue to hold unaltered, but now all the b_n^\pm except b_1^\pm must be regarded as the sum $(b_n^\pm)_1 + (b_n^\pm)_2$ of the contributions of Kratzer's doublet. The theory however gives in addition the ratios $(b_n^\pm)_1/(b_n^\pm)_2$, which must be practically unity except for small values of n . For small values they are slightly uncertain as they depend effectively on the precise distribution of the weight ϖ_m between the equal positive and negative values of m . A study of such doublet intensities might throw further light on Kratzer's theory, and perhaps on the weights themselves.

§ 8. *Summary.*—A general summary of the Correspondence Principle and its "refined" applications is given, with special reference to band-spectra. It is shown that the intensities of the lines in a single band must be expected to obey summation rules similar to those first recognized by Ornstein, Burger, and Dorgelo in atomic spectra. Precise formulæ for the relative intensities are given in terms of the weights for the lines of any band without a zero branch. With the help of particular molecular models the theory can probably be extended to include bands with zero branches. So far as the present rather meagre experimental data can take us, the theory seems to be in agreement with fact. It promises, when better experimental data are available, to provide direct evidence as to the weights of the states of a rotating molecule, and thus fill up an important gap in existing theory. It therefore suggests lines for fruitful experimental work.

In conclusion it is a pleasure to acknowledge the advantages I have derived from opportunities of discussion of these points with Prof. Bohr and Drs. Kramers and Heisenberg, and to tender my best thanks to the International Education Board for contributing so materially to these opportunities.

CXXIX. *The Significance of Spectroscopic Magneton Numbers.*

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◆ 1. *Introduction.*

THE phenomena connected with the multiplet structure of spectral lines and the general Zeeman effect, while extraordinarily complicated, have been empirically co-ordinated in a very satisfactory and coherent manner by the work in particular of Landé and Sommerfeld. While assumed structures of the atom based on the usual quantum theory postulates have been of service in suggesting the kinds of relations to be anticipated, in detail it has proved impossible to deduce the experimentally correct relations as resulting from the properties which the atoms would naturally be supposed to possess. Independently of the fact that half quantum numbers have had to be introduced, the results have seemed to suggest that the ratio of the angular and magnetic atomic moments is by no means always the same, as required by classical quantum theory. To the core of the atom, for example, a double magnetic effect is ascribed. The experimental investigation of the gyromagnetic effect, moreover, has given some ground for the belief that these anomalies are fundamental; and this has led to the view that a basic alteration in the formulation of the quantum theory will be necessary before magneto-spectral atomic effects can be explained.

It seems, however, as though too complete a preoccupation with the complexity of the domain as a whole has rather obscured some of the strikingly "normal" features which emerge from a direct consideration of simpler particular cases. It is these which it is proposed to discuss here. Many of the results are inherent in the treatments of Landé and Sommerfeld; but while they there appear as special cases of anomaly, here they are obtained directly from a more straightforward and natural application of ordinary quantum ideas. In so far as this is possible, it suggests that the general phenomena may eventually be embodied in a scheme which is not purely artificial and formal.

* Communicated by Prof. R. Whiddington, F.R.S.

An outline of the Landé-Sommerfeld systems of classification, and the method of coordination of results based on them, is first given (2), the results being discussed with reference to the formal physical model interpretations which have been used (3). It is shown that an assumption that has hitherto been made tacitly—that mg values correspond to magnetic moments—is justified (4). The simpler cases are then considered, leading to results which agree with what would be expected theoretically (5). These results are applied to the elucidation of the significance of the variation of spectral types across the periodic table (5); and core magnetic moments deduced are correlated with those obtained for ions in solution (6). After some general remarks concerning the occurrence of different relative orientations of the magnetic moments of a core and electron orbit (7), the question of angular momenta and the assignment of inner quantum numbers is briefly discussed (8). Finally the possibility of a magnetic interpretation of multiplet separations is considered, a qualitative explanation being given of the significance of “inverted” terms (9). The paper concludes with a summary (10).

2. The Correlation of the Experimental Observations*.

Spectral terms may be classified by assigning to them a total quantum number, n , an azimuthal number, k , and an inner quantum number, j . For $s, p, d \dots$ terms, k has the values 1, 2, 3 ..., and normally transitions only occur for which k changes by unity. When there is more than one energy level corresponding to a given nk , the terms are differentiated by the inner quantum numbers. In the assignment of these, there is a considerable amount of arbitrariness; but relative numbers may be given quite uniquely if it is assumed, as a fundamental postulate, that transitions only occur (normally) for which $\Delta j = 0$ or ± 1 . The number r will be used to indicate the “permanent” term multiplicity ($r=1, 2, 3 \dots$ for singlets, doublets, triplets ...)—the terms with the smaller k 's usually not having the full number of components. In the following table are given the j values assigned by Sommerfeld on this basis:—

* For fuller details reference may be made to Sommerfeld: *Atombau und Spektrallinien*, Ch. 8 (4th Ed., 1924), and to Back and Landé: *Zeemaneffekt und Multiplettstruktur* (Springer, 1925). Probably the most important papers are:—Landé, *Zeit. für Phys.* xv. p. 189; xix. p. 112 (1923). Sommerfeld, *Ann. der Phys.* lxxiii. p. 209 (1924).

TABLE I.— j values (Sommerfeld).

| Type of Term. | $k \backslash r$ | 1 | 3 | 5 | 2 | 4 |
|---------------|------------------|---|-------|-----------|---------------------------|---------------------------------------------------|
| s | 1 | 0 | 1 | 2 | $\frac{1}{2}$ | $\frac{3}{2}$ |
| p | 2 | 1 | 2 1 0 | 3 2 1 | $\frac{3}{2} \frac{1}{2}$ | $\frac{5}{2} \frac{3}{2} \frac{1}{2}$ |
| d | 3 | 2 | 3 2 1 | 4 3 2 1 0 | $\frac{5}{2} \frac{3}{2}$ | $\frac{7}{2} \frac{5}{2} \frac{3}{2} \frac{1}{2}$ |

The term components may then be distinguished by writing the inner quantum numbers as subscripts, triplet p terms being indicated by p_0, p_1, p_2 . For even series, $\frac{1}{2}$ is added to the j value for convenience, giving p_1 and p_2 for the p doublet terms.

In a magnetic field each nkj term splits up into $2j+1$ equidistant components; and the separation of these from the original position expressed in wave numbers is given by

$$\Delta\nu = mg\Delta\nu_n. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here $\Delta\nu_n$ is the "normal" Larmor separation ($eH/4\pi mc$), m the magnetic quantum number which takes the values $j, j-1, j-2, \dots -j$ for each j term (and hence is integral for odd multiplets, and half-integral for even multiplets), and g the Landé "splitting factor" which may be written as

$$g = \frac{3}{2} + \frac{\left\{ \frac{r}{2} - (k - \frac{1}{2}) \right\} \left\{ \frac{r}{2} + (k - \frac{1}{2}) \right\}}{2j(j+1)}. \quad . \quad . \quad (2)$$

The expression then covers completely the observations on the Zeeman effect in a weak magnetic field for ordinary spectra. (Second degree spectra of the neon type are more complicated and need not be considered at present.)

3. Attempted Physical Interpretations.

Several attempts have been made to interpret the formulæ by picture models of the atom. These differ in detail, but in general type they are similar; all present artificial and formal features, and indicate remarkable anomalies. Sommerfeld's treatment will be briefly outlined.

j is taken as the angular momentum of the atom as a

whole (as a multiple of the unit $h/2\pi$), and is supposed to be the resultant of the vector addition of the moment of the core j_s , and that added by the series electron j_a , these being given by

$$j_s = \frac{1}{2}(r-1), \quad j_a = k-1, \quad r = 2j_s + 1. \quad (3)$$

Possible j values are then given by possible vector combinations of j_s and j_a giving values which are integral or half-integral according to j_s ; the maximum and minimum values being

$$j_{\max.} = j_s + j_a, \quad j_{\min.} = |j_s - j_a|, \quad (4)$$

while for s terms it may be noted that $j = j_s$.

When a magnetic field is applied, m is taken as the resultant angular momentum in the direction of the field. If μ is the magnetic moment of the atom, then

$$m/j = \cos(\mu, H). \quad (5)$$

The change in energy of the configuration in the field is taken as

$$\Delta W = \mu H \cos(\mu, H), \quad (6)$$

so that

$$\Delta \nu = \frac{1}{h} \cdot \mu H \cdot \frac{m}{j},$$

or, expressing $\Delta \nu$ as a multiple of $\Delta \nu_n$, and μ and j as multiples of the Bohr units,

$$\Delta \nu = \frac{\mu}{j} \cdot m. \quad (7)$$

If the ratio between the magnetic and angular moments was constant—that is if both possessed the theoretical values and μ was equal to j —then (7) would be equivalent to $\Delta \nu = m$. Actually $\Delta \nu = mg$, and therefore, on the basis of the above treatment,

$$g = \mu/j. \quad (8)$$

The splitting factor is therefore taken as giving the actual ratio of the magnetic to the angular moment of the atom, as opposed to the theoretical value 1.

Knowing the type of spectrum (and hence the value of r) to which an atom gives rise, it is clear that on the basis of the above equations, using the generalized and empirically correct value of g , the value for μ for an atom in any lj state may be determined, and also its component in the field

direction. In particular, for s terms $\mu = 2j_s$, while the maximum μ is given by

$$\mu_{\max.} = 2j_s + j_a \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In the attempts that have been made to deduce the g formula from the model (taking into account the j_s and j_a precessions about j), it has been taken as an empirical postulate that the core has a double magnetic effect. Working from this Sommerfeld, for example, deduces

$$g = \frac{\mu}{j} = 1 + \frac{j^2 + j_s^2 - j_a^2}{2j^2} \quad . \quad . \quad . \quad . \quad (10)$$

This may be compared with the empirically correct expression which may be written in the form

$$g = 1 + \frac{j(j+1) + j_s(j_s+1) - j_a(j_a+1)}{2j(j+1)} \quad . \quad . \quad (11)$$

It will be seen that, even assuming the core anomaly, the result arrived at is incorrect; which is taken to indicate that two terms (j and $j+1$) must always be considered in deducing the splitting factor for one of them.

In a strong field the separations are always integral multiples of $\Delta\nu_n$, being given, in terms of this unit, following Pauli, by

$$\Delta\nu = \begin{cases} m + j - j_a & \text{for } m \geq j_s - j_a \\ 2m + j - j_s & \text{for } m \leq j_s - j_a \end{cases} \quad . \quad . \quad . \quad (12)$$

An important generalization due to Pauli, which enables corresponding weak and strong mg values to be deduced, and which has been applied and extended by Landé, is the principle of the permanence of the g sums; $\sum g$ or $\sum mg$ taken over all the j 's, for fixed values of r , k , and m , being the same for any field strength. The separations in a strong field, it should be noted, are measured not from each energy level, but from the "centre of gravity" of the whole set of j components of the nk term considered.

From a model point of view, the core and series electron may be supposed to orientate independently. The virtually direct experimental fact that the mg values are integral in itself suggests strongly that the assignment of half quantum numbers to the core and electron has little physical significance. In attempting to derive the formulæ, difficulties similar to those for weak fields are encountered; in particular it seems necessary to attribute double magnetic energy to the core.

4. *The Gerlach and Stern Experiments.*

In the methods of treatment which have been summarized above it has been tacitly assumed that the mg values give a measure of the magnetic moment, and not of the mechanical moment, of the atom in the field direction. Now the change in energy due to the Larmor precession may be written

$$\Delta W = \frac{1}{2}mr^2[(\omega + o)^2 - \omega^2] \\ = mr^2\omega o, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where $o = \frac{eH}{2mc}$. Writing $j' = mr^2\omega$ for the actual mechanical moment, and $\mu' = \frac{er^2\omega}{2c}$ for the corresponding magnetic moment,

$$\Delta W = j'o = \frac{mc}{2e}\mu'o. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Using j and μ for the values as multiples of Bohr units, writing $\Delta W/h = \Delta\nu$, and expressing this in terms of $\Delta\nu_n (= o/2\pi)$,

$$\Delta\nu = j = \mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$\Delta\nu$ is actually given by mg ; but there is no *a priori* reason whatever for supposing that mg gives the magnetic rather than the angular moment, if these do not have their theoretical ratio.

The Gerlach and Stern experiments*, however, justify the assumption made; for in them the magnetic moment of atoms in the field direction is directly measured from the deflexion of a stream of atoms in a non-homogeneous magnetic field. For Ag, Cu, Au, $\mu = \pm 1$, corresponding to the normal s state with $mg = \pm 1$. For Zn, Cd, Hg $\mu = 0$, corresponding to the singlet S state ($mg = 0$). For Tl the separation is much smaller, and in approximate agreement with the value to be expected of the normal state is the p_1 with $mg = \pm 1/3$.

There is thus experimental evidence that the mg values do give the actual magnetic moments of the atoms. Now the j values cannot be found directly: they are assigned primarily in such a way as to provide a simple selection principle for allowable transitions ($\Delta j \neq 1$); and so may have no direct physical significance.

The gyromagnetic effect may be investigated by measuring the angular momentum of reaction due to magnetization of a (ferromagnetic) rod or wire. The ratio between the magnetic moment (M) and the angular moment (J) anticipated is

$$J/M = 2mc/e. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

* *Ann. d. Phys.* lxxiv. p. 673 (1924); lxxvi. p. 163 (1925).

The ratio is found to be constant, and the directions are in agreement with the view that the elementary magnets consist of rotating electrons; but the value of the ratio is exactly half that expected, suggesting that for the atoms or units concerned

$$j = \frac{1}{2}\mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

For atoms in an *s* state this would be anticipated, if Sommerfeld's formulation had definite physical significance; but there is no reason to suppose that the units concerned in Fe, Ni, Co, and Heusler alloys—all of which have been tried—should all be in an *s* state. Actually various values of the ratio, differing from each other, would be expected. At present the gyromagnetic anomaly can hardly be said to justify experimentally the artificial *j* schemes, or to be explained by them; the explanation is probably more straightforward. The anomaly is undoubtedly connected with the fact that atoms with definite magnetic moments exist, and orientation does occur (in accordance with the quantum theory), both of which do not allow of simple explanation on the classical theory.

5. The Simple Cases.

The simpler cases will now be considered, "simple" cases being taken as those in which, from a model point of view, the magnetic moments of the core and series electron are in the same direction, so that the resultant moment of the atom is obtained by the addition of the two constituent moments. For the atoms in the corresponding states, the moments in the field direction will be given by the *mg* values; and these, for the maximum values, are the same whether the core and electron are relatively strongly coupled (weak field) or independent (strong field).

The following table gives the maximum magnetic moments of the atoms in *s*, *p*, *d* states for different multiplicities.

TABLE II.—Maximum magnetic moments.

| Multiplicity. <i>r</i> . | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------------|-----------------------------|---|---|---|---|---|---|---|
| Term type. | <i>s</i> (<i>k</i> =1) ... | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| | <i>p</i> (<i>k</i> =2) ... | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| | <i>d</i> (<i>k</i> =3) ... | 2 | 3 | 4 | 5 | 6 | 7 | 8 |

Now the natural supposition to make is that the magnetic moment of the series electron in a k orbit is actually given by k : a view which the table supports in that μ increases by 1 in passing from s to p to d terms. This assumption enables the magnetic moment of the core (μ_c) to be at once deduced, with the following result:—

Magnetic moment of core.

| | | | | | |
|----------------|----|---|---|---|---|
| r | 1 | 2 | 3 | 4 | 5 |
| μ_c | -1 | 0 | 1 | 2 | 3 |

μ_c is in fact given by

$$\mu_c = r - 2. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

For an atom in any k state the maximum moment is given by

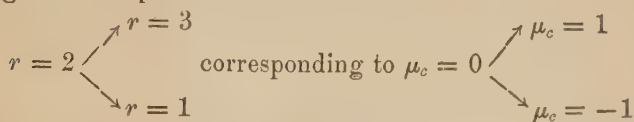
$$\mu_{\max.} = \mu_c + k = r + k - 2. \quad . \quad . \quad . \quad . \quad (19)$$

It is this simple and intelligible feature of the Zeeman effect which it is desired particularly to emphasize.

The deductions expressed in (18) and (19) fit in coherently with the known experimental facts, not only for atoms whose magnetic moments in the normal s state have been directly determined, but also for atom cores whose constitution is known. Doublets occur for Li, Na, K, etc., which consist of a series electron rotating round an inert gas core. Now the inert gases are diamagnetic, and of this the only natural interpretation is that they have no resultant magnetic moment. For Cu, Ag, Au the core, though not of the inert gas type, is a completed configuration in that the M, N, and O IV and V levels respectively are filled up*. Passing on to triplets (Mg, Ca, Sr, etc.) the core has a constitution similar to that of a doublet atom in the s state, so that $\mu_c = 1$. If, however, the outermost core electron rotates in the opposite sense to the series electron, the maximum mg values will all be smaller by 2, this corresponding to the singlet series.

* The upbuilding of atoms is considered with reference to the scheme previously put forward for the distribution of electrons among atomic levels (Stoner, *Phil. Mag.* xlviii. p 719, 1924), which has been discussed and developed by Sommerfeld, particularly in its spectroscopic bearings (*Phys. Zeit.* xxvi. p. 70, 1925). I have since found that the distribution had already been proposed, primarily on the basis of chemical arguments, by Main-Smith. (See 'Chemistry and Atomic Structure,' 1924.) It is very satisfactory that two different lines of attack should have led to the same conclusions.

It thus appears quite natural that an atom consisting of a series electron and a doublet *s* type core should give rise to singlet and triplet series



In proceeding across the periodic table, three remarkable experimental facts emerge :—

- I. The multiplicities are alternately odd and even.
- II. The multiplicities corresponding to any atom are all odd or all even.
- III. The maximum multiplicity observed corresponds to a value of μ_c which is not greater than the number of electrons the core contains in addition to those in the closed configuration with which the period begins.

This may be illustrated by the K-Ni period, for which the spectra have been most fully analysed.

TABLE III.—Observed Multiplicities.
(The most strongly developed are underlined.)

| Element | K | Ca | Sc | Ti | V | Cr | Mn | Fe |
|-----------------------------|----|----------|----------|----------|----------|----------|----------|----------|
| Atomic Number Z... | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 |
| $Z-18-1$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Observed Multiplicities. | | <u>1</u> | | 1 | | | | |
| | 2 | | <u>2</u> | | | | | |
| | | 3 | | <u>3</u> | | | | 3 |
| | | | 4 | | <u>4</u> | | 4 | |
| | | | | 5 | | 5 | | <u>5</u> |
| | | | | | 6 | | <u>6</u> | |
| | | | | | | <u>7</u> | | 7 |
| | | | | | | | 8 | |

For other periods the details are less complete, but there is no disagreement observed with the rules given.

The results then suggest the rather surprising conclusion that the maximum contribution of a core electron to the magnetic moment of the core is 1; this would be expected for electrons added, for example, in s , or p_1 levels (that is in K, L, M, ... I or II levels), but not for those added in other levels for which $j > 1$.

This difficulty, however, partly arises from a too naive extrapolated application of the doublet level classification scheme to the whole process of upbuilding of atoms. That the scheme adopted* for completed configurations is the same as that which applies to doublet systems, rather than any other, has been regarded as somewhat formal and arbitrary; from the point of view of symmetry, however, it seems quite natural. In a doublet atom there is a completed core, and the series electron can occupy any of the levels constituting the next group; energy changes involve transitions of this one electron from any of the possible levels. In a completed configuration all the possible levels are occupied, and energy changes involve transitions of any of the electrons. When atoms are being built up by the gradual addition of electrons, the simple classification of orbits would no longer be expected to apply in its entirety. It is a matter for experiment to decide what scheme will work. The result is the Landé-Sommerfeld system for triplets and multiplets generally. These schemes apply to the atoms as wholes, and give a conspectus of the possible states they can assume. For the classification of orbits in "uncompleted" cores, however, there is as yet no direct evidence; it must be sought on the basis of the experimental rules given above, and by taking into account also phenomena connected with spectra showing different series of k terms with the same multiplicity (normal and "dashed" terms), corresponding to heteromorphic constitutions of the core.

From the observed regularities, it may be said that, for normal spectra, the addition of an electron to the core has the effect of increasing or decreasing its magnetic moment by unity. Further, the fact that atoms may give series with multiplicities differing by two, that is all odd or all even, is due, on the present view, as a first approximation, to a difference in the sense of rotation of one of the core electrons. Thus a core with three electrons in the outer incomplete group would have a magnetic moment of 3, 1, or -1 with $n=5, 3$, or 1. In general it would appear that a core with

* Stoner, *l. c.*

$2n$ outer electrons can have as possible magnetic moments 0, 2, 4 $2n$ (giving multiplicities 2, 4, 6 $2n+2$), and a core with $2n+1$ outer electrons $-1, 1, 3$ $2n+1$ (giving multiplicities 1, 3, 5 $2n+3$). The different core configurations will correspond to different energies and degrees of stability, and so all are not equally probable. Table III., for example, gives an indication of the magnetron number of the core corresponding to the most stable configuration for the conditions under which the spectra are observed, namely, Ca -1 , Sc 0, Ti 1, V 2, Cr 5, Mn 4, and Fe 3.

The possible multiplicities on this view depend solely on the number of "outer" electrons in the core, "outer" electrons being those the core possesses in addition to those forming a completed configuration. The maximum core magnetic moment is equal to this number, and the maximum multiplicity is greater by two. This statement covers both the displacement and branching rules* of Sommerfeld and Landé. It seems to apply not only to "normal" spectra, but also to those of the "second degree," for although the difficulties of the neon spectrum are formidable, in some ways it falls in simply with the above views. Of the 7 outer electrons of the core, the 3 more loosely bound form a secondary outermost group. Multiplicities of 5, 3, and 1, as observed, would be expected. The spectrum thus fits in coherently with the physically significant consequences of the unit magnetic moment idea.

6. Ionic Magnetic Moments.

It seems quite certain that not only atoms or molecules in gases, but also ions in solution tend to take up definite orientations which are determined by quantum conditions. Assuming orientation, the apparent Weiss magnetron number (p) which would be deduced for an ion in solution, using the ordinary Langevin formula, corresponding to whole number Bohr magneton values, may be calculated. The results show that many ions may definitely be characterized by integral magnetic moments; and there are striking regularities in passing across the periodic table, the moment increasing from 0 to 5 in passing from an ion with 18 to one with 23 electrons, and then decreasing to zero for 28 electrons†.

* Back and Landé, *l. c.* p. 55.

† *Atombau*, Ch. viii. p. 637 ff., or Sommerfeld, *Zeit. für Phys.* xix. p. 221 (1924).

(This corresponds to the filling up of the M IV and V sub-levels.) Both in this, and the rare earth group, however, there are anomalies, in that values departing considerably from those corresponding to whole numbers are frequently obtained. Sommerfeld * attributes this to the fact that the calculations are carried out on the assumption that the ions are in an s state, which (apart from the vagueness of the phrase applied to ions) is by no means necessarily true.

The considerations put forward above make it possible to correlate the spectroscopic and ionic moments in a very simple manner; and it seems worth while to do this, although some of the material is familiar.

An ion may be assumed to have approximately the same electronic configuration as an atomic core with the same number of electrons, provided that its resultant charge is the same. Now the fact that atoms can give rise to series with differing multiplicities indicates that the core can assume different magnetic moments; these are not necessarily equally stable, as is shown by the varying prominence of the series of different multiplicities (Table III.). So for an ion there may be different stable configurations; the most stable configuration need not be the same as that of the core with the same number of electrons, firstly because the nuclear charge is in general not the same, and secondly because temperature and other conditions may be widely different. Even if the ionic moments are all integral, there may be an equilibrium distribution between two or more types of ions resulting in apparent non-integral values.

The above remarks will probably serve as sufficient commentary to fig. 1, in which the circles give the possible core magnetic moments deduced as above from the spectra, the crosses the values obtained for ions in solution.

The ionic values † for which the crosses are drawn are given in Table IV., the subscript denoting the charge on the ion.

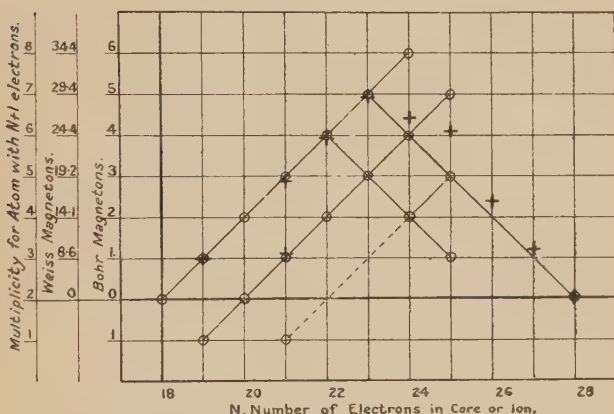
Particularly interesting is the case of V_2 and Cr_3 ; these ions have the same number of electrons, but the stable configurations correspond to different magneton values—very closely to 1 and 3. The fact that Co_2 , Ni_2 , and Cu_2 do not give whole number values suggests that an equilibrium is here concerned.

* *Atombau*, p. 644.

† The data are collected by Dorfmann, *Zeit. für Phys.* xxiii. p. 286 (1924). Papers by Cabrera, *Journ. de Phys.* iii. p. 443 (1922), and Weiss, *ibid.* v. p. 129 (1924), have also been consulted.

A corresponding figure for the rare earths is given. Most of the conclusions which can be drawn from it will be clear on inspection of the curves, and further discussion is of little value until more is known about the spectra. It is

Fig. 1.—Magnetic Moments of Cores and Ions.



⊙ Magnetic moment of core from spectra.

+ Magnetic moment of ion from solution susceptibilities.

TABLE IV.—Ionic Moments.

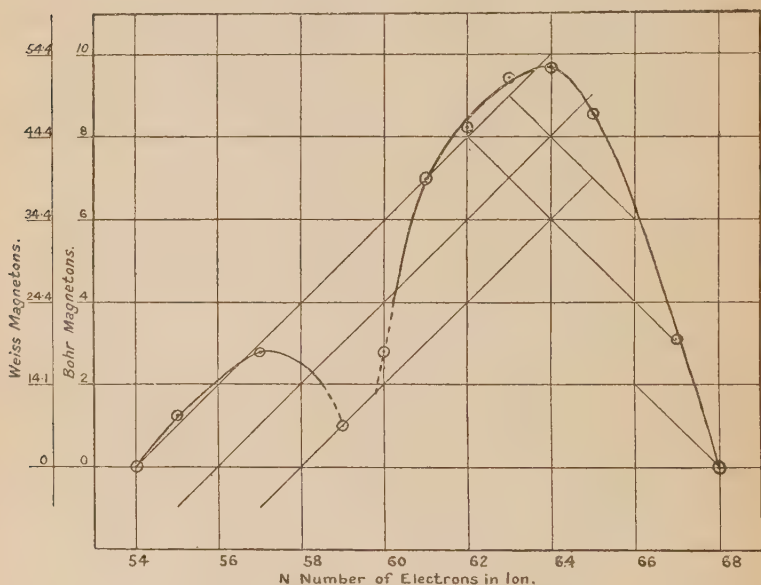
(Expressed in terms of Weiss magnetons.)

| N | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
|-----------|-----------------|-----------------|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ion | Sc ₃ | Ti ₃ | ... | V ₂ | Cr ₂ | Mn ₂ | Fe ₂ | Co ₂ | Ni ₂ | Cu ₂ | Cu ₁ |
| p | 0 | 8.6 | ... | 9.2 | 24 | 29.2 | 26.5 | 25 | 16 | 9.6 | 0 |
| Ion | Ti ₄ | ... | ... | Cr ₃ | Mn ₃ | Fe ₃ | ... | ... | ... | ... | Zn ₂ |
| p | 0 | ... | ... | 18.5 | 24.5 | 28.9 | ... | ... | ... | ... | 0 |

rather remarkable that Gd₃ (N=61), which has been most carefully investigated, with 7 electrons outside a closed configuration, has a magnetic moment very closely corresponding to 7 units (38.65 and 39.82 are values which have been obtained for p).

The straight lines are drawn to bring out clearly the relation of the observed ionic moments with those which might be anticipated, by analogy, for the cores. Since all the ions have the same resultant charge (3), the curve for the ionic moments suggests that the energy values of the N VI and N VII levels, which are being filled with 6 and 8 electrons respectively, are sufficiently far apart to reveal a double process of building up. In the A-Ni curve, however, there is no indication that two different levels (M IV and V) are involved*.

Fig. 2.—Rare Earth Ionic Moments.



The spectra of the rare earths undoubtedly offer an almost inexhaustible field for investigation. It may be noticed that from the ionic moments multiplicities as high as 12 may be anticipated.

7. Some General Considerations.

Except in the cases which have been considered, the magnetic moments of the core and orbit are not in the same direction; in the absence of a magnetic field they are orientated with respect to each other in a manner which

* Cf. Sommerfeld, *Ann. der Phys.* lxxvi. p. 290 (1925).

must be governed by atomic symmetry demands, which are a consequence of the electric and magnetic properties of electrons rotating in orbits. The core and orbit can take up a discrete number of relative orientations, resulting in a discrete number of values for the magnetic moment of the atom as a whole. These are not necessarily integral. When a magnetic field is applied there are a discrete number of possible orientations of the atom as a whole in the field, the number again determined by the symmetry demands characteristic of the configuration involved. The resolved magnetic moments in the field direction are again not necessarily integral, as is proved by direct experiment.

The attempt to force the phenomena into an artificial whole-number scheme seems merely to have added to the difficulties in understanding them. It must be remembered that the idea that the magnetic moment of an orbit in the field direction should be integral was rather a happy guess which enabled an idealized "normal" Zeeman effect to be explained on a quantum theory basis. The normal Zeeman effect observed for singlets involves a core and electron, both with magnetic moments, so that the mechanism concerned is much more complicated than a simple electron orbit. The actual phenomena seem better approached from an experimental standpoint rather than from a theoretical one which is based on a quite arbitrary, even if probable, hypothesis.

From the fact that the difference in energy value of the different magnetic components of a given kj term vanishes with the field, it must be supposed that the relative orientation of the core and orbit is the same for all of them. The triplet p_2 term, for example, in a magnetic field, is characterized by mg values $-3, -3/2, 0, +3/2, +3$; these must be regarded as giving the component of the magnetic moment, 3, in the field direction. For odd multiplicities the mg values are in the ratio $0, 1, 2 \dots$; for even multiplicities $1, 3, 5 \dots$. A direct interpretation is that the values give the directions of the magnetic axes with reference to the field; and that, in effect, a system of axes of symmetry characteristic of the state of the atom is revealed. As would be expected, there is a sharp distinction between the symmetry system characteristic of atoms with odd and those with even numbers of electrons.

Atoms with odd numbers of electrons do not give zero mg values; this is noteworthy, as it indicates that atoms with single unbalanced electron orbits do not set themselves

with the plane of the orbit in the field direction—in agreement with the usual theory excluding such a setting in the simple case of the H atom, for example. When there are two electron orbits, however, as in singlet, triplet . . . systems, the zero mg value does occur, even for configurations with a resultant magnetic moment. It may be suggested that this indicates that the planes of the two orbits concerned do not pass through the nucleus. The whole of the Zeeman effect phenomena indicate the need for a fuller investigation of possible spatial atomic properties of a more far-reaching type than those that have previously been considered. Not only must orientation be taken into account, but also the possibility that the electron orbit planes do not pass through the nucleus.

Even when there is only a single electron associated with a completed diamagnetic core (simple doublet systems), the effects observed are quite different from those anticipated theoretically for a simple electron orbit. For the s term $mg = \pm 1$, and for $p_2(\text{max.})$ $mg = 2$; but considering all the magnetic components, the mg values for p_2 are ± 2 , $\pm 2/3$, and for $p_1 \pm 1/3$. The electron orbit definitely does not set itself so as to give integral moments in the field direction—the presence of the core produces a modification, although it has itself no resultant magnetic moment. This might be attributed to several causes. The series electron might induce a diamagnetic moment in the core, with resultant reaction; this effect, however, would be small, and also would appear in the $mg_{\text{max.}}$ values. It must be remembered, however, that the core, though it has no resultant external moment, gives rise to strong local magnetic fields, and unless the series electron moves with respect to it in a perfectly symmetrical manner, it will show the influence of these fields. The mutual interaction resulting may be the fundamental reason for the observed divergences from integral values in the p_1 case, where the orbit and core have moments not in the same direction; but in the p_2 case there is no escape from the conclusion that there is no necessity for magnetic moments in the field direction to be integral; how far this applies to angular moments cannot at present be decided.

The above remarks are intended to bring out difficulties, in the belief that a clearer realization of them, in as close a relationship as possible to the actual experimental facts, may eventually lead to their being solved. A number of special points will now be briefly discussed.

8. Inner Quantum Numbers.

As has been pointed out, the inner quantum numbers are at present assigned in such a way as to enable a more or less arbitrary selection principle for possible transitions to be satisfied. Although it is quite reasonable to suppose that the j 's so assigned are closely related to the angular moments of the atoms as wholes, there is little justification for interpreting the j 's as giving these directly, unless this leads to a satisfactory physical "model." The Landé, Sommerfeld, and Bohr j values are different. Hicks* has recently pointed out that by adopting a selection principle $j \rightarrow j+2, j, j-2$, and starting from $j=0$ and 1 for odd and even multiplicities, a scheme is obtained which is equally satisfactory; it avoids half-integral j values, and leads to comparatively simple expressions for the splitting factor g .

The angular moment of the atom as a whole, provided it is controlled mainly by the moments of the electrons, should be equal, in the appropriate units, to the magnetic moment; but it cannot be determined directly. Moreover, at present the correct mode of applying theory is too much in doubt to enable the ratios of the magnetic and angular moments of the individual atoms to be deduced from observations on the gyromagnetic effect. The difficulty of the gyromagnetic anomaly must be cleared up before much further progress can be made.

The gyromagnetic effect, however, does certainly suggest that for ions and cores $j = \frac{1}{2}\mu$; for this reason the classification of Landé, which is equivalent to putting $j_{\max.} = \frac{1}{2}\mu_c + k$, using the core values arrived at above, with other values accordingly, has probably the closest relation to reality; moreover, it has the convenience of simplicity, for the term multiplicities, or statistical weights, are then given by $2j$. The physical fact is that only certain transitions occur; but arbitrary j schemes will do little to explain this.

9. Interval Relations and Inverted Terms.

Landé has deduced that the intervals between terms of a multiplet should be in the ratio 1:2:3... for odd, and 3:5:7... for even multiplicities. This holds closely in a number of cases, but the data collected by Hicks† show that in general the agreement is poor, the ratios only serving to give the relative order of magnitude of the intervals.

* Hicks, *Phil. Mag.* xlviii. p. 1036 (1924).

† Hicks, *l. c.*

The relation is deduced on a formal model basis, by attributing to the core and series electron mutual magnetic energy of amount $\mu_c \mu_e \cos \theta$, θ being the angle between the moments; the relative intervals can then be deduced, $\cos \theta$ being derived, again formally, from the constituent j 's involved. The magnetic theory is unable to account satisfactorily for the absolute intervals, these, as is well known, being given very closely by the Sommerfeld relativity formula with an appropriate, admittedly formal, choice of k 's *. The treatment of electron orbits and cores virtually as magnetic shells is, however, very crude, and a closer consideration of the processes involved seems to throw light on some of the difficulties, particularly in connexion with "inverted" terms.

In most of the spectra which have been analysed, the kj components with the highest values of j correspond to the orbits in which the electrons are most loosely bound to the nucleus, the negative energies being smaller. This may be expressed by

$$n_{kj}^r < n_{k,j-1}^r.$$

For inverted terms, on the other hand,

$$n_{k,j}^r > n_{k,j-1}^r.$$

As an example in the Mn sextet system all the D and F terms are inverted. No satisfactory explanation of these inverted terms seems to have been given, though Sommerfeld has pointed out that they occur when the ground term would be a p_2 term, as in N, P, etc.†

Consider a simple idealized case in which the core consists of a nucleus with a single electron going round it. A series electron will suffer magnetic perturbation as it passes through the field of the core. The perturbations will be greatest where the electron is moving with its greatest velocity in regions where the field is strong. For elliptical orbits in general, the energy changes arising from the magnetic perturbations, which control the interval relations, will thus depend mainly on the inner parts of the orbits. The energy corresponding to orbits of different orientations, moreover, will change progressively owing to the change in the field through which the electron passes; but whether the change the electron orbit depends on the extent to which the electron will correspond to an increase or a decrease in the energy of

* Landé, *Zeit. für Phys.* xxiv. p. 88; xxv. p. 46 (1924).

† Sommerfeld, *Phys. Zeit.* xxvi. p. 70 (1925).

penetrates the core; for the field due to the core electron has a different direction inside and outside its orbit.

For complicated cores the details would be exceedingly difficult to work out; but the above considerations may be expected to apply in a general way, and terms may be expected to be normal or inverted according to the extent to which the series electron orbits concerned penetrate the core, or the effective magnetic part of it. If they only penetrate to regions where the field is inverted, the terms will be inverted. Actually the orbit generally passes through both normal and inverted parts of the core field, and the resultant energy change depends on which produces the greater effect, the predominating influence usually being that due to the field where the series electron is moving closest to the nucleus.

The observations may now be considered*. First it may be noted that definitely penetrating orbits give rise to normal terms; and that inverted terms tend to appear for higher azimuthal quantum number orbits (d, f, \dots), and for a given k for higher values of n (corresponding to a relatively greater non-penetrating portion of the orbit). Among the alkali metals, Kd terms are probably inverted, with small intervals; Csd terms are normal, but f terms are inverted. $Na d$ terms are doubtful, but the corresponding $Mg II$ and $Al III d$ terms are inverted. $Ca II d$ terms, and $Ba II f$ terms are normal. It would appear that for similar electron configurations, the higher the nuclear charge, or the higher the resultant core charge, the more persistent is the tendency to "normality"; the extent of penetration roughly corresponds. $Li p$ and d terms, also $B III p$ terms are all normal. This is true also of the p terms of Al, Ga, In, Tl .

At the other end of the periodic table where the cores are smaller, owing to the higher nuclear charge, and where the series electron can be sharply differentiated from the core electrons, inverted terms become much more prominent. Practically all the Fe terms are inverted. The quintet g group is interesting in that $g_2 \dots g_5$ are inverted, g_5, g_6 normal. The main effect on the g_5, g_6 orbits presumably occurs where the electron traverses a normal region of the core field. The Mn octet terms appear to be normal, but the sextet D and F terms are all inverted, as also the P terms with the exception of the first two members. The possibilities of inversion are to be expected in this case, for the sextet core ($\mu_c=4$) has less than its maximum moment,

* The data are collected in Sommerfeld, *Atombau*, p. 685 ff.

owing to the balancing of the magnetic effects of core electron orbits. This will give rise to marked local inverse fields.

With the data available further discussion would be of little value. It seems probable, however, that on the lines sketched out it may be possible to link normal and inverted terms into a single and coherent scheme. "Correct" normal and inverted intervals are of course limiting cases; in between, "anomalous" intervals will occur. The question is connected with that of term magnitudes in general, and in particular with the anomalies occurring in the intervals in passing from lower to higher members of a given series, such as the f series of BaI*, investigated by Saunders. On the whole it seems that the incompleteness in the magnetic explanations of many presumably magnetic spectral effects is due to the extreme difficulties confronting attempts at precise mathematical calculation, rather than to fundamental inconsistencies in the theory itself.

10. *Summary.*

A brief outline is given of the Landé-Sommerfeld schemes coordinating observations on the multiplet structure of spectral lines and their Zeeman effect. The artificial and anomalous features in the attempted physical interpretations are pointed out.

Simple cases are then considered. From these it is concluded that electron orbits and cores are characterized by integral magnetic moments (in terms of the Bohr unit). The magnetic moment of an electron orbit is given by its azimuthal quantum number. The maximum magnetic moment of a core is equal to the number of electrons it contains in uncompleted groups. This determines the maximum term multiplicity (2 greater than the core moment). Magnetic balancing in pairs of core electrons gives rise to lower multiplicities, all odd or all even for odd or even numbers of core electrons.

The magnetic moments deduced spectroscopically are in agreement with those found directly in the Gerlach and Stern experiments, and the core values are simply correlated with the ionic moments deduced from susceptibility measurements.

The question of angular moments, and the assignment of j values is discussed.

* *Atombau*, p. 690.

Finally it is shown that a consideration of the motion of the series electron in the magnetic field of the core leads to a general qualitative explanation of the physical significance of inverted terms, and interval anomalies.

April, 1925.

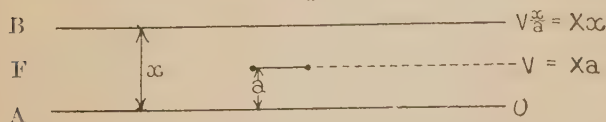
Note added to proof.—In a recent paper on the connexion between the completing of electron groups in atoms with the multiplet structure of spectra, Pauli has discussed in detail, with important conclusions, several questions closely related to those here considered, particularly in section 5. Pauli, *Zeit. für Phys.* xxxi. p. 765 (1925).

CXXX. *Electrical Properties of Neon, Hydrogen, and Nitrogen.* By S. P. McCALLUM, B.A., Hertford College, and C. M. FOCKEN, Rhodes Scholar, Lincoln College, Oxford*.

1. **I**N a recent paper † J. S. Townsend and S. P. McCallum describe an investigation of some of the electrical properties of helium by a new method. This investigation was undertaken primarily to decide by a direct experiment whether there was any appreciable effect due to radiation, comparable with the effect of ionization by collision, during the earlier stages of the development of large currents in gases, and whether the rate of increase of current with increase of potential between the electrodes was the same where the source of electrons was a heated filament and where the electrons were produced by ultra-violet light falling on a silvered plate. This paper describes further investigations with the same apparatus on neon, hydrogen, and nitrogen.

2. A detailed description of the apparatus was given in the paper already mentioned, and we give here only such

Fig. 1.



details as are essential for the understanding of the method used. This involves the measurement of the currents to two silvered plate electrodes A and B (fig. 1).

* Communicated by Prof. J. S. Townsend, F.R.S.

† *Phil. Mag.* xlvii. (April 1924).

A short filament F of fine platinum wire was supported by two silver wires between A and B at a fixed distance a from the lower plate A. The upper plate B was mounted on an axle with a micrometer so that it was capable of adjustment at any distance x from the plate A between 10 and 18 millimetres. A, B, and F were accurately parallel, and the distance a of F from A was 7 millimetres. In each experiment the lower plate A was kept at zero potential; the filament F was maintained at a negative potential V ; the upper plate B was maintained at the negative potential $V \frac{x}{a}$. This establishes

a uniform field $X = \frac{V}{a}$ between the plates except near the filament and its supporting wires. It is important to notice that, when the distance x is changed from x_1 to x_2 and the potential of B from Xx_1 to Xx_2 , there will be no appreciable change in the distribution of the electric force in the space near the filament F and its supporting wires.

The upper plate B was usually adjusted in the experiments at three different distances, and for convenience the distance x was made a simple multiple of the distance a , e.g., $x_1 = 1.5a$; $x_2 = 2a$; $x_3 = 2.5a$. By means of a potentiometer the ratios of the potential of the upper plate B to the filament F could be adjusted very accurately; this is very necessary in determining current-potential curves, as the emission current from a filament is very sensitive to changes in the distribution of the field around it. The filament was heated to a dull red by a battery of large accumulators, and small emission currents of the order of 10^{-12} to 10^{-11} ampere were used, in order to avoid the disturbing effects of large numbers of electrons or positive ions in the field between the plates. With the small currents used the relative values of the currents for different forces were independent of the filament emission. The fall of potential down the filament was about a quarter of a volt, but no appreciable error is made in these experiments by taking the potential of the filament as V .

An induction balance, using a sensitive electrometer as indicator, was used to measure the currents to the plates, and it was arranged so that the ratio of the currents to both the plates could be measured over the same interval of time. This ratio would then be independent of the filament emission, and could be used to check the ratio of the ordinates representing the currents to the two plates obtained with a constant filament emission.

3. The following method was adopted in carrying out the

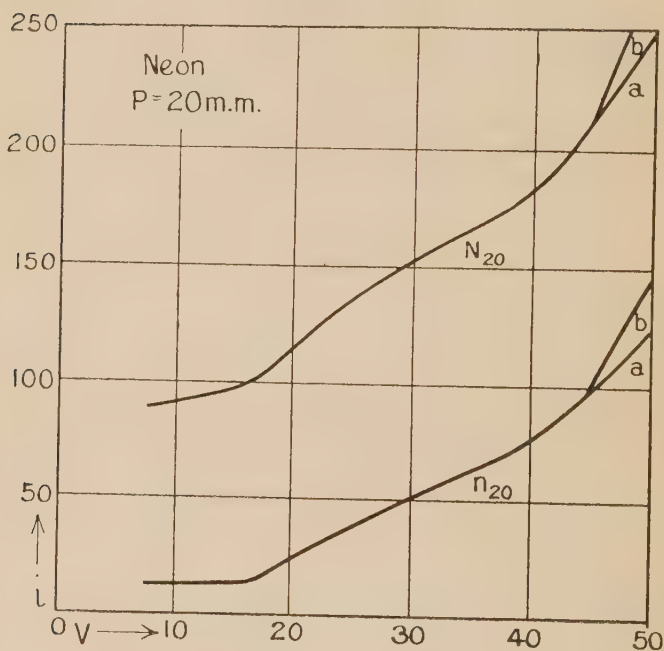
experiments :—The filament was thoroughly glowed out and heated for several hours until the emission had become constant and the positive ions ceased to be emitted. The gas in the apparatus was then pumped out quickly and flushed out with samples of pure gas. A fresh sample at the required pressure was then admitted on which the experiments on conductivity were made. The upper plate B was then set at the distance x , and the potentials of the filament and the upper plate adjusted to V and $V\frac{x}{a}$ respectively. Measurements were then made of the negative currents to the plate A and the positive currents to the plate B for the different values of V . The ratios of the positive and negative currents, obtained during the same intervals of time, were also measured by the induction balance for the different values of V , and the determinations were used to check the ratios of the ordinates of the current-electromotive force curves. The results of these two methods were in very good agreement. The upper plate B was then set at another distance x_2 , and the potential of B was adjusted to $V\frac{x_2}{a}$. The negative

and positive currents for this distance were then measured for the same values of V as were used for the distance x_1 and for the same filament emission. The results of the experiments are given in the form of current-potential curves in which the ordinates represent the currents in arbitrary units and the abscissæ the potential in volts between the filament and the lower plate A, this being the potential through which the electrons, emitted from the filament, fall in passing to the plate A. The curves show the ratio of the positive current to the negative current for each distance x and potential V .

The curves given in fig. 2 represent the results of the experiments with neon at 20 millimetres pressure. Curve N_{20} gives the negative currents to the plate A, and curve n_{20} the positive current to the plate B. The experiments were made with two different distances between the plates $x_1=12$ mm. and $x_2=17.5$ mm. The currents were exactly the same for the two distances, for the smaller potentials of the filament up to 45 volts. For larger potentials from $V=45$ to $V=50$ the currents obtained with the larger distance x_2 were greater than those obtained with the smaller distance x_1 . In fig. 2 the branches of the curves marked a correspond to the distance $x_1=12$ mm., and those marked b to the distance $x_2=17.5$ mm. This increase in the currents with the increase

of the distance corresponds to the effect observed in experiments on photo-electric currents where the rate of increase of the current with the distance between the plates exceeds the rate of increase of the quantity $A\epsilon^{ax}$. As was pointed out in the previous paper, the results of the experiments are completely different from what would be expected if the electrons, emitted from the filament, were capable of exciting radiation in their collisions with the molecules of the gas, which would set free an appreciable number of electrons from

Fig. 2.



the upper plate B. If the increase in the current with potential be due to photo-electric emission from the upper plate B, it is possible to calculate approximately the effect at the two different distances. Thus at the point $V=35$ volts, when x is changed from 12 mm. to 17.5 mm. electrons from the upper plate would have their paths increased in traversing the distance between the plates with an increase of potential along the path of 27.5 volts. The current to the upper plate when $x=17.5$ mm. would then be about twice the current

with the distance $x=12$ mm. But as no difference was observed between these currents, it is evident that any effect due to radiation must be small compared with the principal effect to which the increase of the current must be attributed. Also, on the radiation hypothesis a large continuous discharge should take place with the plates at 17.5 mm. apart when the potential V is about 50 volts; but no such effect was obtained.

Further, it can be shown that at the higher potentials, when the currents between the plates are increased by increasing the distance between the plates, the additional process of ionization rises in importance as X/p increases in the same way as the values of the current i exceed the quantity Ae^{ax} in the experiments with photo-electric currents. This is in accordance with the effect which would result from the ionization of the molecules of the gas by the impact of positive ions or from electrons set free from the negative electrode by the impacts of positive ions, but is not in accordance with the assumption that the effect is due to electrons set free from the negative electrode by radiation from the molecules of the gas.

The neon used in the experiments was very carefully purified by means of charcoal maintained at the temperature of liquid air for about 12 hours. As it was found that the gas was sensitive to traces of impurity, a tube containing charcoal was connected to the apparatus and maintained at the temperature of liquid air during the experiments. The experiments were carried out as soon as possible after fresh gas was admitted to the apparatus, so as to avoid the effect of impurities emanating from the surface of the metal case of the instrument.

A set of curves is shown in fig. 3 for neon at 7 millimetres pressure for two different distances between the plates 12 mm. and 17.5 mm. These curves, the positives being distinguished by the letter n_7 and the negatives by the letter N_7 , coincide up to the point where V is 42 volts, but above that voltage the currents for the larger distance 17.5 mm. are greater than those for the smaller distance 12 mm., the branches being marked b and a respectively.

In the table given below are shown the values of the potential for different pressures at which the curves show appreciable divergence, that is the point at which some process of ionization becomes appreciable, in addition to the ionization by collision of electrons with the molecules of the gas.

Fig. 3.

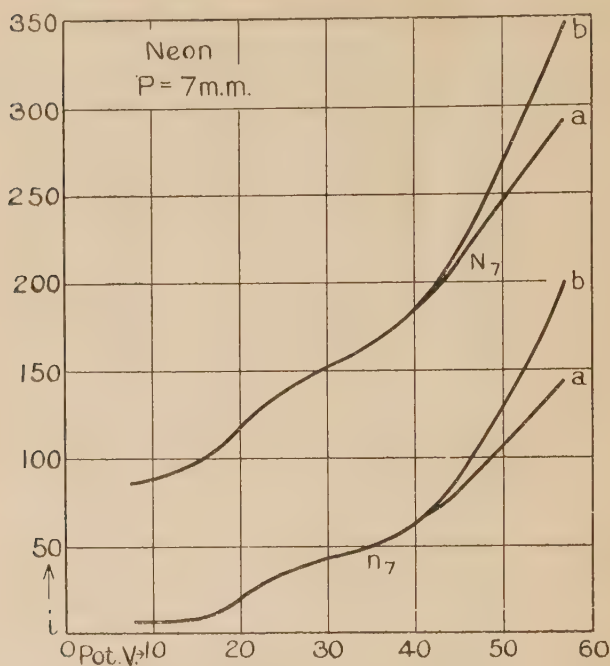


TABLE I.

| p in mm. | V filament potential. | $\frac{X}{p}$ | Potential between plates $V \frac{x}{a}$ ($x=17.5$ mm.). |
|---------------|--------------------------|---------------|--------------------------------------------------------------|
| 20 | 45 volts. | 3.2 | 113 volts. |
| 7 | 42 „ | 8.6 | 105 „ |
| 2.5 | 40 „ | 22.9 | 100 „ |

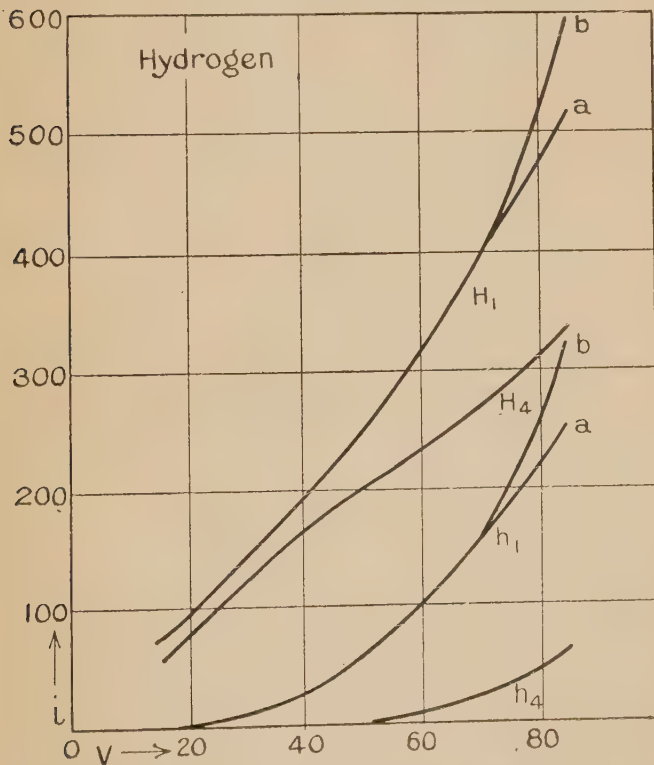
No accurate experiments have as yet been published on the photo-electric currents between parallel plates in neon, but some preliminary experiments we have made show that an additional process of ionization becomes appreciable when $X/p=5.5$ at about 115 volts, and when $X/p=15$ at about 105 volts.

5. Experiments were also made with hydrogen. It was obtained by electrolysis of barium hydrate, and passed through a heated palladium tube into the apparatus. Before

each experiment, pure gas was passed through the apparatus and pumped out so as to remove any impurities which may have been present during the glowing-out of the filament.

The curves in fig. 4 represent some of the results for hydrogen. Curves \bar{H}_1 and \bar{h}_1 show the value of the negative and positive currents to the electrodes A and B respectively in the gas at 4 mm. pressure for different values of V up to 85 volts. Similarly, the curves \bar{H}_1 and \bar{h}_1 represent the

Fig. 4.



results for hydrogen at 1 mm. pressure. With the pressure of 4 mm. the curves obtained for the different values of the distance x from 10.5 mm. to 17 mm. coincided up to the highest value of the potential used, *i.e.* $V=85$ volts, which corresponds when $x=17.5$ mm. to a potential difference between the plates of 212.5 volts and a value of X/p of 30.4. At a pressure of 1 mm. a divergence between the currents was obtained in changing the distance between the plates from 10.5 mm. to 17.5 mm. It became appreciable when

$V=72$ volts, which corresponds to a potential difference between the plates of 180 volts for the largest distance of 17.5 mm. and the value of X/p is 103. The curves giving the positive and negative currents with hydrogen at 1 mm. pressure for the two different distances between the plates of 10.5 mm. and 17.5 mm. are distinguished where they diverge by the letters a and b as in the curves for neon. At a pressure of .53 mm. the divergence between the curves occurred at a lower filament potential, $V=60$ volts, than at the pressure 1 mm. The points at which an additional process of ionization becomes appreciable is shown in Table II.

TABLE II.

| p in mm. | V filament potential. | $\frac{X}{p}$ | Potential between plates V_a^x ($x=17.5$ mm.). |
|---------------|----------------------------|---------------|------------------------------------------------------|
| 1 | 72 volts. | 103 | 180 volts. |
| .53 | 60 „ | 163 | 150 „ |

From determinations of the number of ions generated by collision in hydrogen* we have calculated that the current i between parallel plates first exceeds the quantity $A\epsilon^{ax}$ by an appreciable amount, when the potential difference between the plates is 200 volts for $X/p=88$ and 140 volts for $X/p=175$. These values are in good agreement with those shown in Table II.

6. Some experiments were also made with nitrogen. We are indebted to Mr. Lambert for providing us with a very carefully prepared sample of the gas.

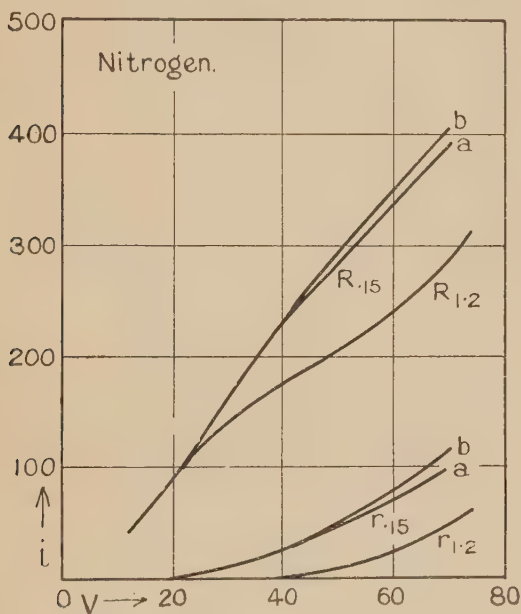
In fig. 5 are shown the curves obtained with two of the pressures used, viz. .15 mm. and 1.2 mm. $r_{.15}$ and $R_{.15}$ represent the values of the positive and negative currents in the gas at .15 mm. pressure, while the letters a and b distinguish the curves (after they diverge) obtained for the currents at the two different values of x of 10.5 mm. and 17.5 mm. It will be noticed from the curves for the pressure 1.2 mm. that no additional process of ionization becomes appreciable for the values of the potential used, *i.e.* up to 185 volts between the plates; but for the pressure .15 mm. the curves show a divergence when $V=46$ volts, $X/p=438$, and the potential difference between the plates is 115 volts. From experiments† on ionization by collision between parallel

* J. S. Townsend, *Phil. Mag.* Nov. 1903.

† H. E. Hurst, *Phil. Mag.* xi. p. 535 (1906).

plates in nitrogen we have calculated that i first exceeds the quantity Ae^{ax} by an appreciable amount when the difference of potential between the plates is 120 volts for $X/p=350$ and 105 volts when $X/p=525$. Here again the results show good agreement.

Fig. 5.

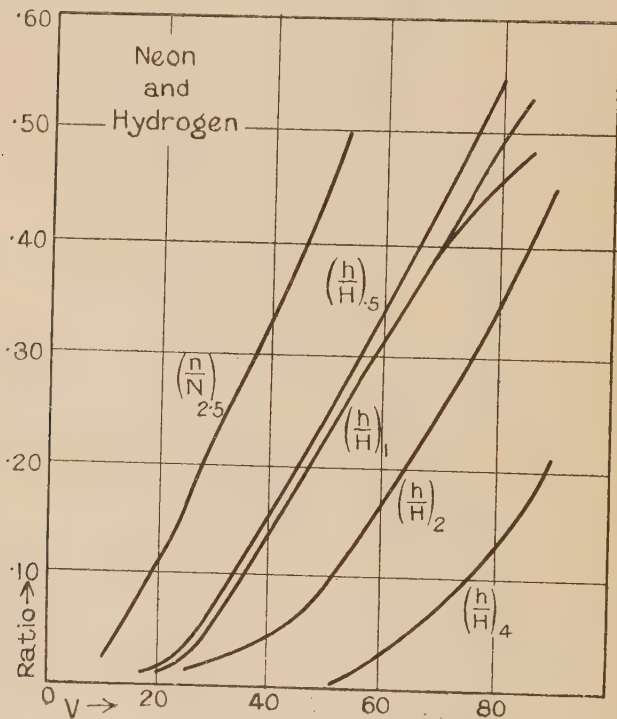


7. In figs. 6 and 7 are plotted the ratios of the positive current to the plate B to the negative current to the plate A for the three gases at different pressures. For example, the curves in figs. 6 and 7 are denoted: in the case of hydrogen at 1 mm. pressure by $\left(\frac{h}{H}\right)_1$, the ordinate at any point giving the ratio of the positive current to the negative current, while the abscissa gives the potential between the filament and the lower plate. Similarly, the curves for neon at 2.5 mm. pressure and nitrogen at 1.2 mm. pressure are denoted respectively by $\left(\frac{n}{N}\right)_{2.5}$ and $\left(\frac{r}{R}\right)_{1.2}$. In order not to complicate the figures, the effect of increasing the

distance between the plates for the higher values of V is shown only in the case of $\left(\frac{r}{R}\right)_{.15}$ and $\left(\frac{h}{H}\right)_1$.

It will be seen from the curves in figs. 6 and 7 that the rate of increase of ionization with increase in electric force ($X=V/a$) is very much greater in neon than in the two diatomic gases hydrogen and nitrogen. Further, in neon

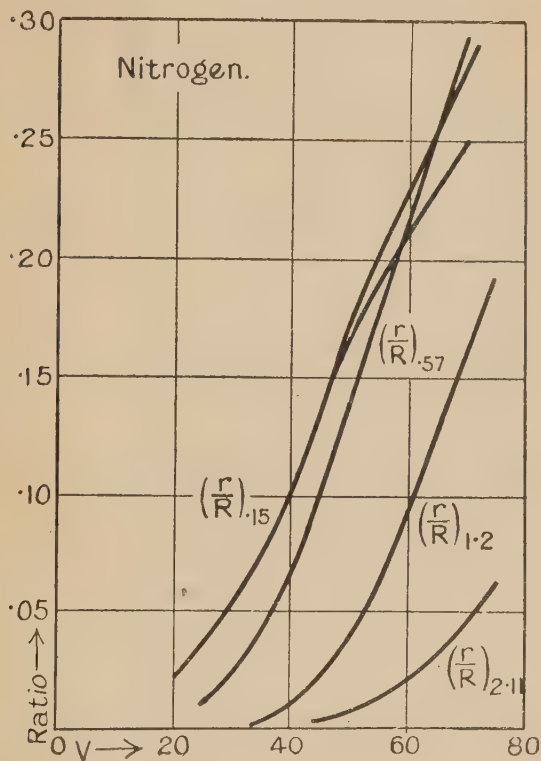
Fig. 6.



as in helium there is only a very small change in the rate of increase of ionization with electric force for large changes of pressure (for example, from 2 mm. to 20 mm. pressure), whereas in the diatomic gases increases from 1 mm. to 4 mm. in hydrogen and from .5 mm. to 2 mm. in nitrogen produce large changes in the electrical conductivity. This is the result to be expected if the electrons lose large amounts of energy in collisions which do not produce ionization, which is in accordance with the results of

other experiments made in this laboratory on the loss of energy of electrons in collision with the molecules of gases.

Fig. 7.



8. The investigation does not indicate the exact cause of the additional ionization which becomes appreciable for the higher values of the electric force, except that it cannot be attributed to the photo-electric action of radiation of a type which has been suggested. Since the effect of the additional process of ionization increases continuously with the ratio X/p , it appears to be due to positive ions which become more active as their velocity increases, or to radiation excited by collisions of electrons when moving with velocities much greater than that required to ionize the molecules of the gas. The experiments show that this action is much larger in monatomic gases than in diatomic gases. In helium it is

appreciable in currents between parallel plates when the potential difference is 108 volts and X/p is 30, and in neon for a potential difference of 105 volts when X/p is 15. But in hydrogen the effect does not become appreciable until the potential difference between the plates is 200 volts and X/p is 88, while in nitrogen it takes place at 210 volts when the ratio X/p is 130. It is probable, then, that the action is due to positive ions, which should lose less energy in collisions which do not produce ionization in monatomic gases than in diatomic gases while falling through the same electric force.

9. The authors wish to thank Professor Townsend for his unfailing interest in the experiments and his ever-ready help and advice.

CXXXI. *Semi-optical Lines in the X-ray Spectra.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the April issue of the Phil. Mag. Messrs. A. Dauvillier and L. de Broglie draw attention to some previous investigations by themselves*, where some of the results given in our paper† are said to be obtained. It seems to us that the ideas underlying their paper are so fundamentally different from ours that there was no reason for giving the reference. Messrs. Dauvillier and de Broglie operate with a system of 6 M and 10 N levels, whereas our conclusions refer to the generally-accepted number of levels, 5 M and 7 N, and to the distribution of the electrons among those levels as given by Stoner‡.

It is, however, interesting to note that Messrs. Dauvillier and de Broglie also, on the basis of their system, find it possible to explain the experimental results given in the diagrams (figs. 1 and 2) of our paper.

Yours sincerely,

E. BÄCKLIN,
M. SIEGBAHN,
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